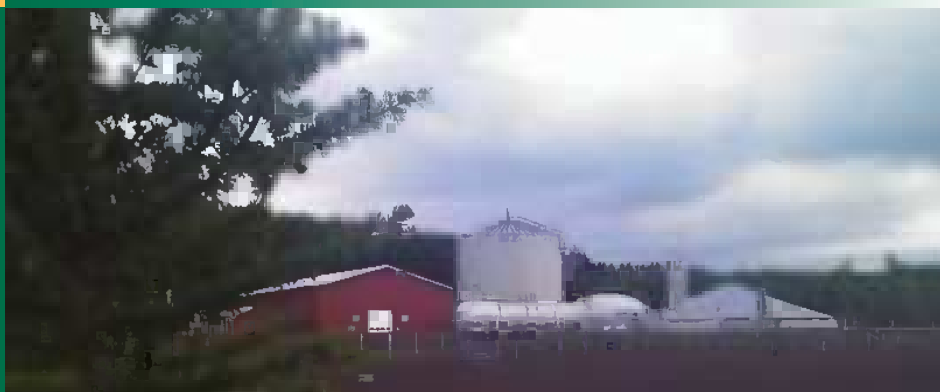
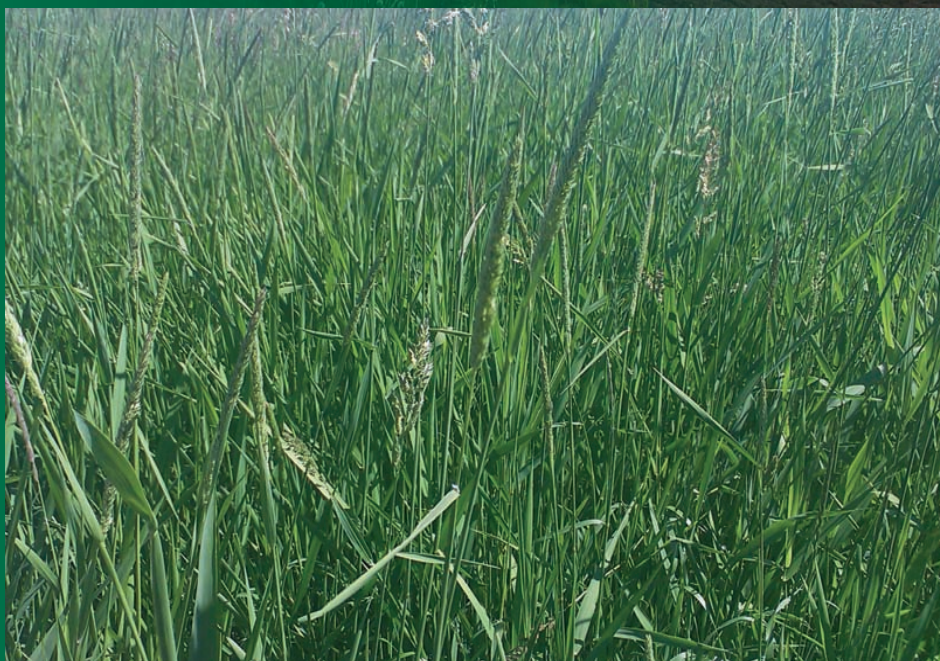




Series: Sustainable Energy Developments **4**



Technologies for Converting Biomass to Useful Energy



Editor: Erik Dahlquist

TECHNOLOGIES FOR CONVERTING BIOMASS TO USEFUL ENERGY –
COMBUSTION, GASIFICATION, PYROLYSIS, TORREFACTION
AND FERMENTATION

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Sustainable Energy Developments

Series Editor

Jochen Bundschuh

University of Southern Queensland (USQ), Toowoomba, Australia

Royal Institute of Technology (KTH), Stockholm, Sweden

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Technologies for Converting Biomass to Useful Energy

Combustion, gasification, pyrolysis, torrefaction and fermentation

Editor:

Erik Dahlquist

*School of Sustainable Development of Society and Technology,
Malardalen University, Högskeplan Vasteras, Sweden*



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Renewable energy sources and sustainable policies, including the promotion of energy efficiency and energy conservation, offer substantial long-term benefits to industrialized, developing and transitional countries. They provide access to clean and domestically available energy and lead to a decreased dependence on fossil fuel imports, and a reduction in greenhouse gas emissions.

Replacing fossil fuels with renewable resources affords a solution to the increased scarcity and price of fossil fuels. Additionally it helps to reduce anthropogenic emission of greenhouse gases and their impacts on climate change. In the energy sector, fossil fuels can be replaced by renewable energy sources. In the chemistry sector, petroleum chemistry can be replaced by sustainable or green chemistry. In agriculture, sustainable methods can be used that enable soils to act as carbon dioxide sinks. In the construction sector, sustainable building practice and green construction can be used, replacing for example steel-enforced concrete by textile-reinforced concrete. Research and development and capital investments in all these sectors will not only contribute to climate protection but will also stimulate economic growth and create millions of new jobs.

This book series will serve as a multi-disciplinary resource. It links the use of renewable energy and renewable raw materials, such as sustainably grown plants, with the needs of human society. The series addresses the rapidly growing worldwide interest in sustainable solutions. These solutions foster development and economic growth while providing a secure supply of energy. They make society less dependent on petroleum by substituting alternative compounds for fossil-fuel-based goods. All these contribute to minimize our impacts on climate change. The series covers all fields of renewable energy sources and materials. It addresses possible applications not only from a technical point of view, but also from economic, financial, social and political viewpoints. Legislative and regulatory aspects, key issues for implementing sustainable measures, are of particular interest.

This book series aims to become a state-of-the-art resource for a broad group of readers including a diversity of stakeholders and professionals. Readers will include members of governmental and non-governmental organizations, international funding agencies, universities, public energy institutions, the renewable industry sector, the green chemistry sector, organic farmers and farming industry, public health and other relevant institutions, and the broader public. It is designed to increase awareness and understanding of renewable energy sources and the use of sustainable materials. It aims also to accelerate their development and deployment worldwide, bringing their use into the mainstream over the next few decades while systematically replacing fossil and nuclear fuels.

The objective of this book series is to focus on practical solutions in the implementation of sustainable energy and climate protection projects. Not moving forward with these efforts could have serious social and economic impacts. This book series will help to consolidate international findings on sustainable solutions. It includes books authored and edited by world-renowned scientists and engineers and by leading authorities in economics and politics. It will provide a valuable reference work to help surmount our existing global challenges.

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Marta Irene Litter	(advanced oxidation technologies, heterogeneous photocatalysis), Gerencia Química, Comisión Nacional de Energía Atómica, San Martín, Prov. de Buenos Aires, Argentina & Consejo Nacional de Investigaciones Científicas y Técnicas, Buenos Aires, Argentina & Instituto de Investigación e Ingeniería Ambiental, Universidad de General San Martín, Prov. de Buenos Aires, Argentina

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Thomas Ludwig	(green(-ing) computing, energy-efficient high-performance computing), University of Hamburg, Hamburg, Germany
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This book is dedicated to my wife Christina and my children Katarina, Emma and Gustaf

–Erik Dahlquist

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Contributors

Suresh K. Aggarwal	University of Illinois, Chicago, USA, ska@uic.edu
Thorsten Ahrens	IBU – Institut für Biotechnologie und Umweltforschung, Ostfalia University, Wolfenbuettel, Germany, th.ahrens@ostfalia.de
Kalyan Annamalai	Texas A&M University, College Station, TX, USA, kannamalai@tamu.edu
Anna Behrendt	IBU – Institut für Biotechnologie und Umweltforschung, Ostfalia University, Wolfenbuettel, Germany, anna_behrendt@yahoo.de
Sharad Bhartiya	Department of Chemical Engineering, Indian Institute of Technology Bombay, Powai, Mumbai, India, bhartiya@che.iitb.ac.in, sharad_bhartiya@iitb.ac.in
Wlodzimierz Blasiak	School of Industrial Engineering and Management, Division of Energy and Furnace Technology, Royal Institute of Technology (KTH), Stockholm, Sweden, Blasiak@kth.se
Erik Dahlquist	School of Sustainable Development of Society and Technology, Mälardalen University, Västerås, Sweden, erik.dahlquist@mdh.se
Umberto Desideri	Perugia University, Perugia, Italy, umberto.desideri@unipg.it
Changqing Dong	School of Energy & Power Engineering, North China Electric Power University, Beijing, China, cqdong1@163.com, dongcq@ncepu.edu.cn
Adeola Ijeoma Eleri	Renewable Energy Department, Energy Commission of Nigeria, Abuja, Nigeria, adeola.eleri13@gmail.com
Klas Engvall	Department of Chemical Engineering and Technology, Chemical Technology, Royal Institute of Technology (KTH), Stockholm, Sweden, kengvall@kth.se
Francesco Fantozzi	Perugia University, Perugia, Italy, francesco.fantozzi@unipg.it
Xiaoying Hu	School of Energy & Power Engineering, North China Electric Power University, Beijing, China, xiaoying_826@163.com
Efthymios Kantarelis	School of Industrial Engineering and Management, Division of Energy and Furnace Technology, Royal Institute of Technology (KTH), Stockholm, Sweden, ekan@kth.se
Rodrigo A. Labatut	Department of Biological and Environmental Engineering, Cornell University, New York, USA, ral32@cornell.edu
Torbjörn A. Lestander	Swedish University of Agricultural Sciences, Unit of Biomass Technology and Chemistry, Umeå, Sweden, torbjorn.lestander@slu.se
Shi-Zhong Li	Institute of New Energy Technology, Tsinghua University, Beijing, China, szli@mail.tsinghua.edu.cn

Bernt Lie	Telemark University College, Porsgrunn, Norway, Bernt.Lie@hit.no
Truls Liliedahl	Department of Chemical Engineering and Technology, Chemical Technology, Royal Institute of Technology (KTH), Stockholm, Sweden, truls@ket.kth.se
K.P. Madhavan	Department of Chemical Engineering, Indian Institute of Technology Bombay, Powai, Mumbai, India, kpmadhvan@iitb.ac.in
Yrjö Majanne	Department of Automation Science and Engineering, Tampere University of Technology, Tampere, Finland, yrjo.majanne@tut.fi
Anders Nordin	Energy Technology and Thermal Process Chemistry, Umeå University, Sweden, anders.nordin@chem.umu.se
Martin Nordwaeger	Energy Technology and Thermal Process Chemistry, Umeå University, Sweden, martin.nordwaeger@chem.umu.se
Ingemar Olofsson	Energy Technology and Thermal Process Chemistry, Umeå University, Sweden, ingemar.olofsson@chem.umu.se
Linda Pommer	Energy Technology and Thermal Process Chemistry, Umeå University, Sweden, linda.pommer@chem.umu.se
Bale V. Reddy	Faculty of Engineering and Applied Science, Institute of Technology, University of Ontario, Oshawa, ON, Canada, bale.reddy@uoit.ca,
Marc A. Rosen	Faculty of Engineering and Applied Science, Institute of Technology, University of Ontario, Oshawa, ON, Canada, marc.rosen@uoit.ca
Dejan Vasilic	IBU –Institut für Biotechnologie und Umweltforschung, Ostfalia University, Wolfenbuettel, Germany, dejan.vasilic@oestfalia.de
Weihong Yang	School of Industrial Engineering and Management, Division of Energy and Furnace Technology, Royal Institute of Technology (KTH), Stockholm, Sweden, weihong@kth.se

Foreword

A good environment and at the same time good economic living conditions—that is the goal for us as well as for our children and their children. To achieve that we need sustainable energy resources that do not harm the environment through pollution of water, air and food. At the same time we need food and thus should not compete between food and use of resources for other purposes.

Biomass resources is one of the key resources we have that can both give us the energy we need, the food we demand and also be a feed stock for many kind of products we use daily like paper, packages, furniture, plastic, chemicals etc. Estimates made from statistics on use of land area for agriculture, forestry or just more extensive use indicates a biomass production of approximately 270,000 TWh/year, which should be compared to the total global energy use of approximately 140–150,000 TWh/year. As we also have huge amounts of solar and wind power potential, and already have explored a lot of our hydro power resources, there should principally be no problem to build a sustainable society without fossil fuels, although the distribution of resources is not always matching the demands locally or even regionally.

The major concern thus would be to use the biomass resources we have in best possible way. Conversion methods thus are important to refine. We could just burn the wood over an open fire, and then have a net efficiency of less than 10% between higher heating value of the wood compared to the energy taken up by the water you want to boil. Or we could use the biomass as fuel in a combined heat and power plant with exhaust gas condensation, where the corresponding efficiency as heat plus electricity would be 117%, which is common in Scandinavia.

In China the majority of the energy used for electricity production comes from coal. Installed capacity for electricity production from biomass is forecasted to increase from 5500 MW_e in 2010 to 13,000 MW_e in 2015. 8000 MW should come from agricultural waste, 2000 MW from biogas and 3000 MW from municipal solid waste. The total available resources of biomass still are much higher. They amount about 690 million tonnes of straw, 840 million tonnes manure from live-stock, 3 million tonnes food waste for biodiesel, and 950 million tonnes solid industry waste. If all this could be used for energy purpose it could replace about 1000 million tonnes coal, or some 7000 TWh/y. The main question then is how to do this in a sustainable way. Many different technologies would be needed. Easy to decompose biomass could be fermented to give biogas, but at the same time also give good fertilizer back to the farm land. More difficult materials can be combusted or gasified thermally. Ash might be brought back to at least forestry. The same wood could first be used as building material, furniture or paper boxes, and then be used as an energy resource in a power plant when the function as building material is over. Food waste can be used where manure or house hold waste is fermented in a biogas plant, etc. There are many technologies available, and many of them are covered in this book on biomass conversion with examples from all over the world.

Concerning the biomass resources these differ between different climate zones and soil types. Still, there is a major potential to enhance the production everywhere by introducing good conditions like enough water, nutrients and new more resistant species of the crops with respect to insects, fungus etc. The potential can be seen by comparing the production as tonne product per hectare 1970 compared to today. In middle income economies and high income economies, the production has approximately doubled during this time period, while it has increased by some 50% in low income economies, according to statistics from the United Nations for 213 countries. Still, there is a major gap between both the middle income economies and the high income economies, and even larger compared to low

income economies. A review of resources and crops used in different climatic zones, as well as new possibilities to use crops efficiently in e.g. biorefineries are covered in this book.

Yang Yong-Ping,
Professor, Vice President of North China Electric Power University
Director of National Engineering Laboratory for Biomass Power Generation Equipment
Member of National Energy Expert Advisory Committee

Editor's Foreword

150 years ago the modern world was developing as a consequence of cheap and easily accessed energy from fossil fuels. Together with this resource engineers developed new technologies for converting the fuels into useful products like mechanical power, electricity and heat. Today we are facing a situation where cheap fossil fuel is becoming more scarce, and the oil price has gone from around e.g. US\$ 20/barrel in the mid-19th century to around US\$ 100–110/barrel in 2012. Coal is principally still relatively cheap, but environmental concerns with respect to global warming as well as other negative impacts from spreading dust and sulfur are alarming. In August 2012 we heard that the Arctic ice cap is smaller than it has been for several thousand years. It is as small as the previous smallest size in 2007 already in August, while the minimum takes place in September. Heavy storms are causing problems in the USA and East Asia. The previous stable weather patterns are becoming unstable and unpredictable, probably as a main consequence of the global warming caused by emission of primarily CO₂ from fossil fuel combustion. To avoid this effect we need to use renewable energy instead, and this as fast as possible. Here we have hydro power, wind power and solar power, but first of all Bioenergy, which can be both stored over the seasons as well as converted into all energy forms we need for heat and power, transportation and as a base chemical for manufacturing of anything from plastics and soap to buildings. As biomass is also food needed for a growing population, we need to look at biomass from a holistic perspective, where e.g. the cereal grain should be used primarily for food while the straw and other agricultural waste should be used for the other applications. To do this a number of different conversion techniques are needed.

The purpose of this book is to give a concise overview of all major conversion techniques for biomass. We start with thermal conversion and follow with torrefaction, biogas production using biological methods and finally mechanical processes like briquetting and pelletizing.

Combustion, biogas production using microbiological methods and polarization are already used extensively, while gasification, pyrolysis and torrefaction are still under development. Some countries are utilizing biomass a lot while others very little. In Sweden 1/3 of all primary energy used is as biomass, or 132 TWh/y out of a total 400 TWh/y 2010 (when we exclude the waste heat from nuclear power plants). That is one of the highest percentages in developed countries, while many still developing countries may have similar or even higher figures, at least if we include also biomass collected and used locally.

From a future perspective biomass could replace most of our energy needs if it was utilized in a most efficient way. Still, the use must be in a sustainable way. Here for instance it is important to see that organic material and nutrients like phosphorus and nitrogen are recirculated to farmland, and thus biogas production is good from a system perspective. The organic residues then will be a fertilizer to keep the production high in the long term, but we also have to see that we do not bring negative substances from anaerobic digestion into the food, and precautions have to be made. On the other hand some materials like wood are not very suitable for biogas production and here gasification and combustion are more suitable. We can also produce ethanol from pre-treated cellulosic material like straw, and then it is useful to combine it with biogas production of the residual brine. Also pyrolysis to replace oil and torrefaction to replace coal are new alternatives. All these aspects are highlighted in this book.

If we just look at EU27 I have tried to estimate the total annual biomass production from the data on crops grown and areas used for agriculture and forestry. The rough figures come to around 8500 TWh/y biomass produced. A very small portion of this is really utilized for our different needs. If we could use e.g. straw efficiently for biogas production or for production of ethanol using fermentation

we could produce most of the fuels needed for our vehicles. By introducing a series of hybrid electric vehicles the total energy for transportation could be decreased by roughly 70–80%, where half would be as electricity, and the rest as methane, ethanol or bio-diesel. The electricity then could be produced in CHP plants using biomass as the fuel, aside from wind power, hydro power and solar power.

To make this economically attractive still we need to have good conversion techniques, and these will be the focus of this book. If we can combine these conversion techniques with robust agriculture and forestry, and reuse materials in a most efficient way, we can see a bright future without fossil fuels. The advantage also would be a solution to the upcoming climate problems with global warming. This is the motivation for this book.

The book is using SI units as the standard. Still, SI units can have different forms as well. It is common to use MJ (million Joules) for energy in SI units, but as kWh, (kilo watt hours), MWh (mega watt hours), TWh (terra watt hours) and toe (tonne oil equivalents) are used by e.g. UN and the World Bank for energy these units have been used as well. One toe is approximately 10 MWh. For electric power usually MW has been used. China is using t.c.e (tonne coal equivalent) for energy as well, and in a few places this unit has been used relating to Chinese energy data. For surface area ha (10,000 m²) and km² (100 ha) have been used concerning calculations related to production of different crops, yield, etc. Both m³ (1000 liters) and liters have been used for volume. Concerning pressure this is MPa in SI, but as bar is very common also this is used. Parts per million, or ppm is also used commonly, and thus also is used here and there in the book, although kg/kg is the SI sort. Where it is used in the book is just because it is difficult to change in some already produced diagrams and similar. Both kg and tonnes have been used as well, where we refer to metric tonne (tonne = 1000 kg). Sometimes also other units like Pg for weight (10¹⁵ g) and TJ (10¹² J) for energy are used, and probably will be used even more in the future.

The authors are all well established in different fields of biomass conversion and also cover most parts of the world. This book is written in parallel with volume 3 in this book series on sustainable energy developments, where biomass resources are presented.

Erik Dahlquist
January 2013

About the editor



Erik Dahlquist with a TPV module for combined heat and electric power in small biomass fired boilers

Erik Dahlquist is currently Professor in Energy Technology at Malardalen University (MDU) in Västerås, Sweden. His focus is on biomass utilization and process efficiency improvements. He started working at ASEA Research in 1975 as engineer in analytical chemistry related to nuclear power, trouble shooting of electrical equipment and manufacturing processes. In 1982 he started with energy technology within the pulp and paper industry and participated in the development of year-around fuel production from peat. In 1984 ASEA started a company ASEA Oil and Gas with a focus on off-shore production systems. One area was waste water treatment and separation of oil and water. He then became technical project manager for development of a Cross Flow Membrane filter. This led to the formation of ABB Membrane Filtration. The filter is now a commercial product at Finnish Metso Oy under the name Optifilter. As part of this development work he started as an industrial PhD student at KTH and received his doctorate in 1991. In 1989 he became project leader for ABB's Black Liquor Gasification project, which resulted in a number of patents. From 1992 to 1995 he was department manager for Combustion and Process Industry Technology at ABB Corporate Research. He was also at that time member of the board of directors for ABB Corporate Research in Sweden. From January 1996 to 2002 he was General Manager for the Product Responsible Unit "Pulp Applications" worldwide within ABB Automation Systems. The product area was Advanced Control, Diagnostics, Optimization, Process Simulation and Special Sensors within the pulp and paper industry. During 1997–2000 he was part time adjunct professor at KTH and from 2000 to 2002 part time professor at MDU. He has been responsible for research in Environmental, Energy and Resource Optimization at MDU since 2000. During 2001–2007 he was first deputy dean and later dean of the faculty of Natural Science and Technology. He has been a member of the board of the Swedish Thermal Engineering Research

Institute division for Process Control systems since 1999. He received the ABB Corporate Research Award 1989. He has been a member of the board of SIMS (Scandinavian Simulation and Modeling Society) since 2003 and deputy member of the board of Eurosims since 2009. He has been a member of the editorial board of the Journal of Applied Energy, Elsevier since 2007. He is also a member of the Swedish Royal Academy of Engineering (IVA) since 2011. He has 21 (different) patents and approximately 170 scientific publications in refereed journals or conference proceedings with referee procedure to his name. He has published seven books, either as editor or author.

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Erik Dahlquist
January 2013

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CHAPTER 1

An overview of thermal biomass conversion technologies

Erik Dahlquist

The major thermal biomass conversion techniques are combustion, gasification, pyrolysis, and torrefaction. Combustion means 100% oxidation of all organic contents of the fuel using air/oxygen, while gasification means partial combustion where some 15–30% of the oxygen is added in relation to what would be needed for 100% oxidation. In pyrolysis we only heat but without adding air and thereby gaseous components of the organic material are evaporated and later condensed as liquid hydrocarbons. Torrefaction is when you do partial pyrolysis but only to remove some of the gaseous components, where the purpose not is to produce liquid hydrocarbons but make a compact residue that can replace coal in coal fired power plants. Only combustion is really used on a large scale commercially today for biomass, although significant work has been done on development of the other techniques as well. The hurdle has been the cost as the fossil alternatives with natural gas, oil and coal have been “too cheap”. As different type of penalties are introduced on fossil fuels to compensate for the costs caused by environmental impact like greenhouse effects and acidification, the relative competitiveness will change. As the new technologies are improved they will also be cheaper, and with new system designs we can foresee a commercial expansion within the next coming 10 years also with respect to all other technologies apart from combustion. Several countries like the USA, Denmark, Finland, Germany, the Netherlands and Sweden all have strategies for research and demonstration of biomass for multiple uses such as for production of plastics, textile fibers, and many different chemicals (Andersson, 2012).

Already today, significant amounts of biomass are converted mostly into heat. The estimate is that approximately 13% of all global primary energy utilized is biomass. Still, most of this is converted with very low efficiency technologies like burning in an open fire. Then the efficiency from fuel to useful heat for e.g. cooking food is just around 10%. By introducing simple ovens the efficiency may then be increased several times, and by introducing very efficient cogeneration technologies the sum of heat and electric power in relation to the heating value of the biomass fuel may even be 117% in e.g. Sweden. This is actually quite common in the large-scale CHP (combined heat and power) plants in Sweden, where we have a heat demand at least most time of the year. In hot climates, the alternative is CCP, combined cooling and electric power production. The efficiency then can be quite high, although not as high as in Scandinavia, where also condensate heat can be utilized from the exhaust gas to reach the 117%.

In China, approximately 15% of the coal is gasified today and coal is used in the production of 50% of all chemicals. In 2005, China produced 232,820,000 tonnes of coke, 8,950,000 tonnes of calcium carbide, 25,000,000 tonnes of chemical fertilizer and about 3,500,000 tonnes of methyl alcohol from coal. Shenhua Baotou coal to olefin program has a production of 1.80 million tonnes/year; coal-to-carbinol is 600,000 tonnes/year. There are more than 10,000 coal gasification stoves in operation in China. Fixed-bed gasifiers are the most common. In ammonia-fertilizer industries, the number of water-coal gasifiers exceeds 4000 units; there are also more than 5000 two-phase gasifiers where e.g. Lurgi gasifiers are used for producing industrial fuel gas (Yasuyuki, 2007). Here the potential for gasification of biomass should be very high, as there are major resources of straw just being wasted today. As gasification is already common, it should be easier to get acceptance also for biomass gasification. Still, there is a demand for the right incentives like price or regulatory directives. Torrefaction also has a major potential, as the product is compact and easy to transport long distances in an economic way. The heating value may be up to 25 MJ/kg dry substance (DS), which is in the same range as coal. Another advantage is that the

pellets or briquettes produced from torrefied biomass can be used in normal coal mills without having to modify the grinding equipment normally used for the coal. This makes it easy to start using biomass as a complement to coal on a large scale.

Gasification can be used to produce different type of chemicals. Either methane can be produced and separated directly, or the syngas with $\text{CO} + \text{H}_2$ is converted through catalytic processes to different chemicals using e.g. the Fischer-Tropsch process. An alternative can be to heat biomass without introducing air, and we then get pyrolysis instead of gasification. Then a more complex mixture of gaseous and liquid components is produced. This can be refined in a way similar to how crude oil is refined in refineries. This technology is now being developed both “on its own” and as part of gasification systems. For example, CORTUS has a process where biomass is first pyrolysed and the pyrolysis gas is then combusted to heat the char, which is gasified using steam (<http://www.cortus.se/>, 2012). Chalmers in Gothenburg is also working with a similar technology together with Metso Power. Andritz is working with the Carbona process and several companies in among others Japan are working on processes with gasification combined with combustion in two separate fluidized beds. Here the char is combusted to produce heat for the gasification and to get rid of the residual char coal. A pilot torrefaction plant in Örnsköldsvik also is using pyrolysis gas for heating and driving the torrefaction, although using lower temperatures than are normally used in pyrolysis.

Aside of these thermal conversion processes we have microbial processes as well as mechanical compaction in different ways. Concerning microbial processes, in China these can be from small batch fermenters in single households to produce gas for cooking food to large scale plants like Tianguan’s biorefinery in Nanyang (Henan Tianguan Enterprise, 2012), where $150 \times 10^6 \text{ m}^3$ gas will be produced annually.

The processes are of batch type as well as continuous and the temperature can be from room temperature over mesophilic around 35°C to thermophilic around 55°C . In all these processes the basic principles are still the same. We use different types of microorganisms to convert biomass through biochemical process routes into something that is more valuable for us as humans than only CO_2 .

In combined systems, we can see that it would make sense to use easily decomposable substances like house hold waste for biogas production, while dry, solid waste is better to convert in the thermal conversion processes. An advantage with the microbial processes is both that all nutrients like P, N and K can be recirculated to farmland after the processing, and also there will be an organic residue that has the properties to keep moisture in the soil when distributed on farmland. As the organic content has a tendency to decrease rapidly today with a lot of cereal production and less animals, this is of high importance in many countries and should be taken into account in many more in the future, to create a sustainable agriculture. To make it possible to recycle the organic material on the other hand we need to be careful with what we put into the reactors. This is especially true in wastewater treatment plants, where many different chemical substances may come to the plant like pharmaceuticals, tensides, oil, etc. Thus, we can foresee a major demand on separation of waste and avoidance of disposing toxic chemicals into waste and wastewater in the future. The complete material handling system will be integrated with the energy system.

In reality, we will need to recycle also the inorganics from the thermal conversion plants to sustain the productivity in forestry and other areas long term. Here we have just started, and have a very long way to go until we reach sustainability.

Concerning the mechanical conversion techniques the major focus is on robustness, so that the equipment and tools will last and not need replacement too frequently. For that reason e.g. briquetting may be easier than pelletizing, as the friction surface is smaller.

For pyrolysis the major difficulty is that we get a process that gives a different composition depending on what we put in. The chemical composition is affecting the liquid phase composition a lot, and if we want to produce a very homogeneous product, we have a problem. Still, by measuring the chemical composition of the biomass we put in we can to some extent control the process in such a way that we can get more homogeneous results. This is also relevant for the

optimization of combustion, gasification, and biogas production processes. In this book, we cover these aspects especially looking at NIR (near infrared spectroscopy) and RF (radio frequency) sensor systems, which are introduced for on-line applications to determine moisture content and chemical composition of biomass. Several installations are done by e.g. Bestwood for this in Sweden.

This chapter only has the aim to give a very broad overview of the different technologies and you will read more about everything in the rest of the book. Thus only a few references have been included, as more comes in later chapters instead.

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CHAPTER 2

Simulations of combustion and emissions characteristics of biomass-derived fuels

Suresh K. Aggarwal

2.1 INTRODUCTION

There is worldwide interest in developing renewable energy sources in a sustainable manner. This is motivated by our excessive reliance on finite fossil energy sources, environmental concerns due to greenhouse gas emissions, and ever-growing energy needs especially due to emerging economies and population growth. A sustainable and carbon-neutral energy future will require a significant broadening of our energy portfolio and reducing reliance on non-renewable sources. While multiple renewable energy sources and technologies will be needed to attain this goal, non-food and regional fuel sources, especially biomass, are expected to play a major role in this effort. Biomass represents one of the primary energy resources in the world after coal and oil, particularly in developing countries (Hall *et al.*, 1991). It refers to a broad variety of feedstock ranging from agricultural waste, such as straw, bagasse, rice husks, olive pits, and nuts, to energy crops such as miscanthus and sorghum (Werther *et al.*, 2000). It also includes algae, forestry waste such as wood chips, bark and thinning, and other solid wastes including sewage sludge, as well as municipal waste. The use of biomass would not only reduce our dependence on fossil energy sources, but also provide energy in a sustainable and carbon neutral manner.

Biomass can be converted to more valuable energy forms *via* a number of processes including biological, thermal, and mechanical or physical processes. Figure 2.1 from Gill *et al.*,

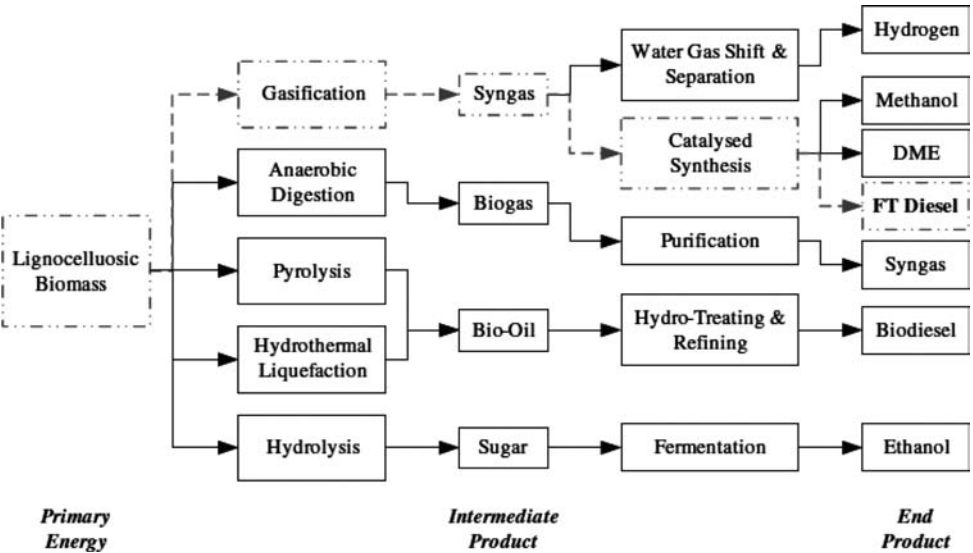


Figure 2.1. A schematic of various conversion methods and major fuels produced from biomass (Gill *et al.*, 2000).

(2000) provides a schematic of the various conversion processes and major products (fuels) from lignocellulosic biomass.

Biological conversion faces many challenges due to high cost and low efficiency, and is currently limited with regards to feedstock and products (Lin *et al.*, 2006). In contrast, thermochemical methods have been extensively investigated for the conversion of biomass to a variety of products, such as energy, fuels, and chemicals. This chapter starts with an overview of thermochemical conversion processes, namely direct biomass combustion, pyrolysis and gasification. A brief discussion of various processes involved and fuels produced is provided. This is followed by a discussion of research dealing with biomass-derived fuels. The focus is on the combustion and emission characteristics of syngas and biogas. Both the fundamental and applied research is reviewed. Finally, some research needs are outlined.

2.2 THERMOCHEMICAL CONVERSION PROCESSES

This section provides a brief overview of the thermochemical processes, namely, direct combustion, pyrolysis, and gasification, for converting biomass to useful energy, chemicals, and fuels.

2.2.1 Direct biomass combustion

Direct biomass combustion has traditionally been used to supply heat and power in the process industry. However, such systems for electricity generation have low overall efficiency and emit significant pollutants (Caputo *et al.*, 2005). Systems utilizing direct combustion of agricultural waste include kilns and boilers for generating steam used for various industrial applications including electricity production. Werther *et al.* (2000) provide a review on direct biomass combustion. Figure 2.2 from their paper shows a schematic of processes associated with the combustion of wood or straw.

The sequence of events which a lump of solid fuel undergoes during combustion includes heating up, drying, devolatilization, ignition and combustion of volatiles, and finally the combustion of char. As discussed by Werther *et al.* (2000), the fundamental information required to characterize the combustion of agricultural residues include temperatures at the start of devolatilization and char combustion, the influence of drying on the devolatilization process, the composition of devolatilization products, and the effect of volatile release and combustion on the overall combustion process.

There are many operational and environmental challenges associated with the biomass combustion technology. These include the low bulk density of agricultural waste (~5–10 times lower than coal), high moisture content, low melting point of the ash, and high content of volatile matter. The low density leads to problems such as high volume required for storage, low energy output on a volume basis, and high transportation costs. Densification is often used to address these problems. Similarly, the low melting temperature of the ash leads to problems such as bed agglomeration in a fluidized bed, and fouling, scaling and corrosion of heat transfer surfaces. The higher content of volatile matter implies significant differences between the combustion and emission characteristics of agriculture biomass and fossil fuels (Ogada *et al.*, 1996). For instance, the presence of volatile matter enhances the biomass ignitability and reactivity, but the combustion process becomes difficult to control. This presents challenges in using agriculture biomass in the existing combustion devices. Moreover, due to the presence of sulfur, nitrogen, chlorine etc., the biomass combustion leads to the formation of gaseous pollutants such as SO_x , NO_x , N_2O and HCl. Many of these issues can be addressed in biomass co-fired combustion systems (Backreedy, 2005), but the amount of biomass is generally limited to 5–10% of the total feedstock due to concern about the plugging of existing feed systems (Yoshioka *et al.*, 2005). Further discussion of these issues can be found in Werther *et al.* (2000).

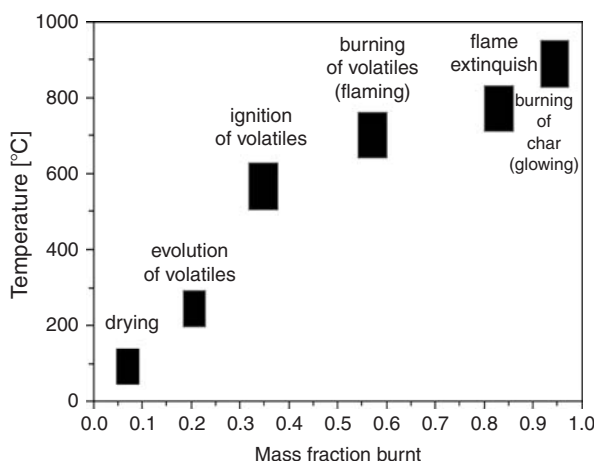


Figure 2.2. A schematic of various processes associated with the combustion process of a lump of straw or wood chip (Werther *et al.*, 2000).

There are few fundamental studies, experimental or theoretical, dealing with the biomass combustion and emission characteristics. This may partly be due to the lack of information about the physical and chemical properties of various biomass feed stocks. Consequently, there has not been as much work on the development of reliable kinetic and thermo-transport models for investigating biomass combustion and emissions. Such information is of critical importance for the design and efficient operation of biomass-based combustion systems. The lack of this information has also been a factor in low utilization of direct biomass combustion compared to biomass pyrolysis and gasification. Thus, there is a need for more fundamental research on biomass combustion, and the development of a database on the physical and chemical properties of biomass feed stocks. As such information becomes available, along with appropriate kinetic and thermo-transport models, the existing software, which has developed for the simulation of coal combustion (Smith *et al.*, 1990), may be modified for predicting the biomass combustion and emission characteristics. Subsequently, these tools can be further refined for optimizing and improving the performance of direct biomass combustion systems.

2.2.2 Biomass pyrolysis

Biomass pyrolysis refers to thermal decomposition in the presence of little or no oxygen, while biomass gasification involves pyrolysis and partial oxidation in a well-controlled oxidizing environment. Depending on the process variables, such as the reactor temperature and residence time, the biomass pyrolysis yields various amounts of gaseous, liquid, and solid products of varying compositions. For instance, conventional pyrolysis, which has been utilized for thousands of years, involves lower temperatures and longer residence times with the principal product being the solid char. In contrast, fast pyrolysis involves moderately high temperatures ($\sim 500^{\circ}\text{C}$) and short residence times (~ 2 s), with the main product being a dark brown liquid or bio-oil along with other gaseous, liquid and solid products, including char. This process is much more commonly used at present compared to conventional pyrolysis. While most agricultural and forestry residues can be used in fast pyrolysis, most work has focused on wood-based feedstock, including hemicellulose, cellulose and lignin. The pyrolysis process generally requires about 15% of the energy available in the feed, which can be provided by the combustion of char or a combination of char gasification and combustion of resulting producer gas. Note that char and gas are the two main by-products of pyrolysis, which typically contain about 25 and 5% of the energy in the

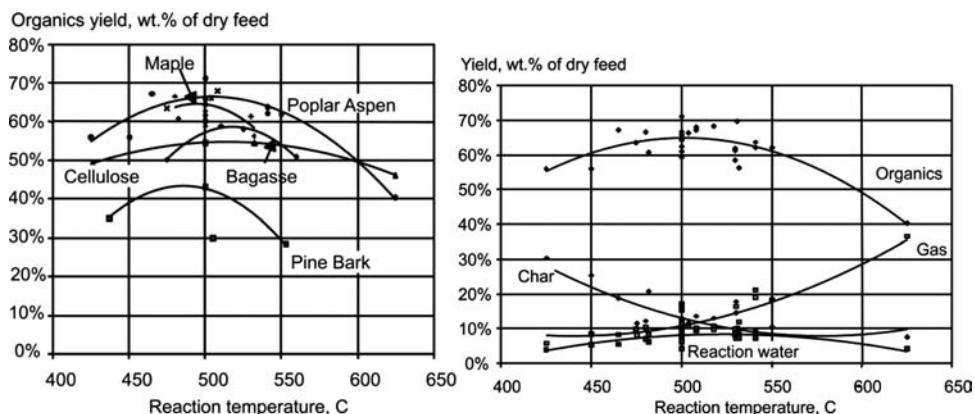


Figure 2.3. (a) Organics yield from different feedstocks, and (b) variation of products from aspen poplar with temperature (bottom) (Bridgwater, 2011).

feed, respectively. Other means of supplying the required energy may include the combustion of bio-oil, fresh biomass, or fossil fuel, depending upon the reactor design and regional conditions.

Bridgwater (2011) and Mohan *et al.* (2006) provide reviews on fast pyrolysis and the properties of bio-oils generated from this process. The effects of various process parameters on the overall reaction rate, volatile yields and products formed are extensively discussed in these reviews. Such parameters include the biomass composition and structure, reactor temperature, heating rate, and residence time. Various gaseous and liquid fuels produced from bio-oils are also discussed. As stated earlier, fast pyrolysis in general involves high heating rates with a reaction temperature of around 500°C, rapid cooling of the pyrolysis vapors to yield bio-oil, which is the main product, and a rapid removal of product char to minimize cracking of vapors. It is characterized by the strongly coupled processes of heat and mass transport, phase change, and chemical kinetics. As discussed by Bridgwater (2011), a critical factor is to bring the reacting biomass particles to an optimum temperature and minimize their exposure to lower temperatures that favor the formation of charcoal. While there have been studies on the kinetic and thermal decomposition mechanisms for the pyrolysis of plant biomass, various processes associated with fast pyrolysis are generally not well understood.

The major product of pyrolysis is a dark brown liquid or bio-oil, which has approximately the same elemental composition as the original biomass. It consists of a complex mixture of oxygenated hydrocarbons with a varying but appreciable amount of water from both the original moisture and reaction product. Note that the presence of water makes bio-oils immiscible with petroleum-derived fuels. The physical properties of bio-oils are discussed in Czernik (2004). Proximate analysis of the bio-oil gives a chemical formula of $\text{CH}_{1.9}\text{O}_{0.7}$. The typical heating value of bio-oils is about 17 MJ/kg, which is about 40–45% of that of hydrocarbon fuels. Figure 2.3a from Bridgwater (2011) shows typical organics yields from different feedstocks and their variation with temperature, while Figure 2.3b shows the temperature dependence of the four main products, namely organics, char, gas, and water, from a typical feedstock.

In addition, Bridgwater (2012) lists the physical properties of a representative wood-derived bio-oil. The pyrolysis chemistry of different biomass feed stocks is discussed in Bridgwater (2012). Bio-oils can be utilized in several different ways to produce energy, fuels, and chemicals. They have been used directly as fuels in stationary applications, especially for electricity generation. A more sustainable approach is to produce conventional fuels for transportation and power generation using either an integrated facility or a decentralized operation. Such fuels include diesel, gasoline, kerosene, methane, liquefied petroleum gas, and others. An integrated facility involves a refinery-like operation with biomass pyrolysis followed by preprocessing, deoxygenation, and refining of

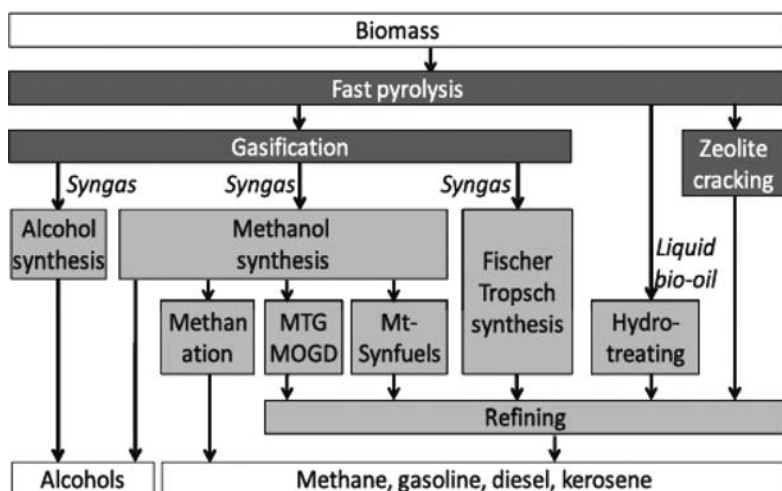


Figure 2.4. Schematic of a refinery for the production of various biofuels and chemicals (Mohan, 2006).

bio-oils. A schematic of such a facility is depicted in Figure 2.4 from Mohan (2006). As discussed in this reference, the decentralized operation has received much interest in recent years. In such an operation, bio-oils or bio-oil-char slurries produced from biomass pyrolysis are transported to a central processing plant for gasification and synthesis of hydrocarbon transport fuels, such as Fischer-Tropsch (FT) fuels and alcohols. While there is some energy penalty associated with transportation and additional bio-oil gasification, it may be compensated by the economy of scale that can be achieved in a gasification and fuel synthesis plant on a commercial scale.

The modeling of pyrolysis processes is extremely complex (Niksa, 2000) due to the wide variation in biomass composition and the amount and number of products formed. Most previous work has focused on developing empirical or global kinetic models for predicting the rate of production of various species, including char, bio-oil, liquids, and other liquid and gas species, formed during pyrolysis. Varhegyi *et al.* (2011) performed thermo-gravimetric experiments to examine the pyrolysis of different feedstocks, and reported a distributed activation energy model using three pools of reactants. Brown *et al.* (2001a, b) studied experimentally and numerically the chemistry of biomass and cellulose pyrolysis in a laminar entrained-flow reactor using a molecular-beam mass spectrometer. Computational fluid dynamics (CFD) simulations were performed to model the transport and chemical processes in the reactor. It was observed that the primary cellulose pyrolysis products underwent subsequent secondary reactions. A rate law was developed to describe the thermal conversion of these products. While such studies have provided valuable information on the overall pyrolysis kinetics, there is scope for more fundamental research using surrogate mixtures to examine the transport and thermochemical processes associated with the biomass pyrolysis and subsequent conversion of bio-oil to fuels. Significant research is also needed on catalytic processes for the production of various gaseous and liquid fuels.

In summary, the potential of using biomass pyrolysis and subsequent refining of bio-oils to produce second-generation biofuels is increasingly being recognized. Similar to a petroleum refinery, a biorefinery concept may provide a sustainable and value-added approach for the use of biomass to produce energy, fuels and chemicals. This concept is particularly attractive for biomass because of its chemical heterogeneity and regional variability. However, the chemical composition of biomass, approximately $(\text{CH}_2\text{O})_n$, is quite different from that of petroleum, $(\text{CH}_2)_n$, and, therefore, the range of primary chemicals derived from biomass and petroleum will be different. In (Bridgwater, 2011) a schematic of an integrated pyrolysis-based biorefinery concept is shown. It indicates that bio-oils produced from pyrolysis can be processed to provide various gaseous and liquid fuels. These fuels are mostly compatible with conventional fuels, but are cleaner.

Consequently, they can be deployed without significant changes to existing infrastructure. Moreover, as discussed in the next section, the biomass gasification can be used to make syngas, a mixture of H_2 and CO , for subsequent synthesis of hydrocarbons, alcohols and other chemicals. However, this route may be quite energy intensive, and its cost effectiveness and environmental benefits need to be examined. It may be more economical to use syngas directly for electricity generation.

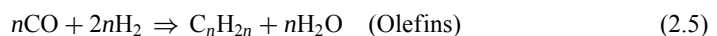
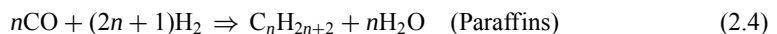
2.2.3 Biomass gasification

Biomass gasification involves pyrolysis and partial oxidation in a well-controlled oxidizing environment. It leads to products, such as H_2 , CO , CO_2 , H_2O , and hydrocarbon species. The heat required for biomass drying, heating and pyrolysis is provided by the partial oxidation of biomass. Gasification is deemed as the most promising technology for producing renewable and carbon-free energy, as it provides tremendous flexibility with regards to feedstock and the fuels produced. In general, the gasification process converts low value biomass to a gaseous mixture containing syngas (mixture of H_2 and CO) and varying amounts of CH_4 , and CO_2 . It can also produce hydrocarbons, particularly in the lower temperature range. The oxidizing agents can be pure O_2 , air, steam, CO_2 or their mixtures. The syngas composition can be varied by using air and steam as the gasification agent (Rapagna, 2000). Moreover, the presence of CO_2 can be used to increase H_2 and CO contents, as it transforms char, tar and CH_4 into H_2 and/or CO in the presence of a catalyst such as Ni/Al (Ollero, 2003). Table 2.1 from (Jones *et al.*, 2003; Giles, 2003) lists the representative compositions and properties of syngas used in various Integrated Gasification Combined Cycle (IGCC) facilities. As indicated, syngas has a wide composition range due to a large variety of source materials and processing techniques.

Numerous studies have been reported in recent years, dealing with the type of reactors used for gasification, thermo-chemical processes involved, and various gaseous and liquid fuels produced during gasification. Wang *et al.* (2008) and Gill *et al.* (2000) provide reviews of work on biomass gasification. As discussed in these reviews, significant advances have been reported in biomass gasification technology and syngas utilization. The syngas can be used to generate heat and power, for example, in an IGCC facility (Rodrigues *et al.*, 2003), produce H_2 (Watanabe, 2002), and synthesize other chemicals and liquid fuels such as F-T fuels (Tijmensen, 2002). Gill *et al.* (2000) summarize the various routes for the utilization of syngas, including the production of F-T and other transportation fuels. As discussed by Gill *et al.* (2000), the global reactions associated with syngas formation from biomass (CH_n) include:



Reaction (2.1) corresponds to syngas formation in the presence of O_2 , while reaction (2.2) is the well-known water-gas-shift-reaction and reaction (2.3) is associated with the steam reforming of methane. Reactions (2.2) and (2.3) are used to control the H_2/CO ratio. The production of F-T fuels from syngas involves a series of reactions in the presence of a catalyst. The global reactions for this process can be written as:



The first step during F-T formation is the conversion of syngas into $-CH_2-$ alkyl radicals and H_2O . The $-CH_2-$ alkyl radicals then combine in a catalyst reaction to produce synthetic paraffin and olefin hydrocarbon (HC) fuels of various chain lengths. The amount and type of fuels formed are determined by parameters such as temperature, pressure, H_2/CO ratio, and the type of catalyst. In general, F-T fuels can be produced from a variety of solid, liquid, and gaseous sources, and

further processed to yield clean transportation fuels with desired specifications. Gill *et al.* (2000) provide an overview of technologies, including Biomass-to-Liquid (BTL) and Coal-to-Liquid (CTL) Gas-to-Liquid (GTL) processes, for producing various fuels through gasification and F-T processes.

Regardless of feedstock or process, F-T fuels have a number of desirable properties. For example, F-T diesel fuels can be produced with a high cetane number, with ultra-low sulfur and aromatic content, with the consequence of improved engine performance, significantly lower particulate mass (PM) emissions and favorable NO_x/PM trade-off. However, these fuels generally have poor lubricity and lower volumetric energy density. These shortcomings can be alleviated by blending these fuels with petro-fuels. Thus, the biomass gasification can be used to produce syngas and subsequently clean drop-in transportation fuels. The effects of F-T fuel properties on engine performance and emissions have been reported by a number of investigations (Abu-Jrai *et al.*, 2006; Schaberg *et al.*, 2005; Wu *et al.*, 2007). Gill *et al.* (2000) illustrate the improved HC/NO_x tradeoff achieved with advanced injection timing using the GTL fuel compared to petro-diesel and rapeseed methyl ester (RME) biodiesel fuels.

2.3 SYNGAS AND BIOGAS COMBUSTION AND EMISSIONS

Syngas can be produced using a variety of feedstocks and conversion processes, particularly using gasification, as discussed in the preceding section. On the other hand, biogas is generally produced by anaerobic digestion or fermentation of biodegradable materials in an oxygen-free environment (<http://en.wikipedia.org/wiki/Biogas>). There is significant potential for using syngas and biogas fuels for transportation and power generation. Both of these fuels represent a clean and renewable energy source, and offer great flexibility in their production and utilization. The next two sections provide an overview of the fundamental and applied research dealing with these fuels.

2.3.1 Syngas combustion and emissions

Syngas is a renewable energy source with wide flexibility in feedstock and conversion processes. Most of the harmful contaminants and pollutants can be removed in the post-gasification process prior to combustion. Moreover, technologies for its production and utilization are fairly developed, as several IGCC plants are currently operational around the world. There is also significant interest in using syngas as a transportation fuel. In addition, the use of syngas in fuel cells, such as solid oxide fuel cells, through the reforming of hydrocarbons and other routes is also being explored (Kee *et al.*, 2005; 2008).

Considerable work has been reported on syngas combustion and emissions (Lieuwen, 2009; Cheng *et al.*, 2009). Fundamental studies have focused on various aspects, including the development of thermo-transport and kinetic models, and examining the ignition and combustion characteristics. A major challenge identified in these studies is due to a substantial variation in its composition and heating value. This requires that the syngas combustion and emission behavior be analyzed for a wide range of composition. Thus, properties such as adiabatic flame temperature, laminar burning velocity, flammability limits, flame stability, extinction, and blowout need to be determined for a wide range of syngas composition. This presents challenges while designing syngas combustors, requiring optimization for locally available fuels. As indicated in Table 2.1 (Kee *et al.*, 2005), the main components in syngas are H₂ and CO, with varying amounts of diluents, such as CO₂, H₂O, and N₂, as well as CH₄ in small amounts. Consequently, previous studies on syngas combustion have considered several representative compositions. Table 2.2 lists an average syngas composition, based on the values in Table 2.1.

Fundamental combustion properties can be analyzed by starting with the stoichiometric mass balance for a syngas-air mixture as:

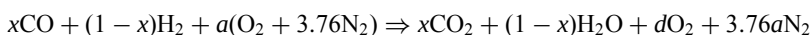


Table 2.1. Representative compositions (in terms of percentage of mole fractions) and related properties of syngas utilized in various IGCC plants; from Kee *et al.* (2005).

Syngas	PSI	Tampa	El Dorado	Pernis	Sierra Pacific	ILVA	Schwarze Pumpe	Sarlux	Fife	Exxon Singapore	Motiva Delaware	PIEMSA	Tonghua
H ₂	24.8	37.2	35.4	34.4	14.5	8.6	61.9	22.7	34.4	44.5	32.00	42.30	10.3
CO	39.5	46.6	45.0	35.1	23.6	26.2	26.2	30.6	55.4	35.4	49.50	47.77	22.3
CH ₄	1.5	0.1	0.0	0.3	1.3	8.2	6.9	0.2	5.1	0.5	0.10	0.08	3.8
CO ₂	9.3	13.3	17.1	30.0	5.6	14.0	2.8	5.6	1.6	17.9	15.80	8.01	14.5
N ₂ + Ar	2.3	2.5	2.1	0.2	49.3	42.5	1.8	1.1	3.1	1.4	2.15	2.05	48.2
H ₂ O	22.7	0.3	0.4	–	5.7	–	–	39.8	–	0.1	0.44	0.15	0.9
LHV [(Btu/ft ³)]	209	253	242	210	128	183	317	163	319	241	248	270.4	134.6
LHV [kJ/m ³]	8224	9962	9528	8274	5024	7191	12492	6403	12568	9477	9768	10655	5304
T _{fuel} F/C	570/300	700/371	250/121	200/98	1000/538	400/204	100/38	392/200	100/38	350/177	570/299	338/170	–
H ₂ /CO ratio	0.63	0.8	0.79	0.98	0.61	0.33	2.36	0.74	0.62	1.26	0.65	0.89	0.46
Diluent	Steam	N ₂	N ₂ /Steam	Steam	Steam	–	Steam	Moisture	H ₂ O	Steam	H ₂ O/N	N ₂	n/a
Equivalent	150	118	113*	198	110	–	200	–	*	116	150	129	134.6
LHV [Btu/ft ³]													
Equivalent	5910	4649	4452	7801	4334	–	7880	–	–	4600	5910	5083	5304
LHV [kJ/m ³]													

*Always co-fired with 50% natural gas.

Table 2.2. Average composition and standard deviation based on syngas mixtures listed in Table 2.1.

Syngas constituent	Average [% vol]	Standard deviation [% vol]
H ₂	31.0	14.9
CO	37.2	11.0
CH ₄	2.2	2.9
CO ₂	12.0	7.7
N ₂ + Ar	12.2	19.7
H ₂ O	7.8	14.1

Table 2.3. Heating values and adiabatic flame temperatures of various syngas mixtures.

H ₂ mole fraction	CO mole fraction	Mol. weight [kg/kmol]	Heating value [kJ/kg]	Heating value [kJ/kmol]	Adiabatic flame temp ($\Phi = 1.0$) [K]
0	1	28.0	10100.5	282814.0	2394.2
0.1	0.9	25.4	11145.3	283090.6	2385.1
0.2	0.8	22.8	12428.3	283365.2	2381.6
0.3	0.7	20.2	14041.3	283634.3	2379.3
0.4	0.6	17.6	16130.2	283891.5	2377.8
0.5	0.5	15.0	18942.6	284139.0	2376.9
0.6	0.4	12.4	22932.9	284368.0	2377.8
0.7	0.3	9.8	29036.9	284561.6	2379.3
0.8	0.2	7.2	39539.4	284683.7	2381.6
0.9	0.1	4.6	61871.7	284609.8	2385.1
1	0	2.0	141794.1	283588.2	2386.7

Here x defines syngas composition in terms of the mole fraction of CO, a , is related to the equivalence ratio Φ ($\Phi = \text{AF}_{\text{stoichimetric}}/\text{AF}_{\text{actual}}$ with $\text{AF} = m_{\text{Air}}/m_{\text{Fuel}}$ = air to fuel ratio) through the relation $a = 1/(2\Phi)$, and d represents the excess O₂ (for $\Phi < 1.0$), given by $d = (1 - \Phi)/(2\Phi)$. Air is assumed to contain 21% O₂ and 79% N₂ by volume. The above equation can easily be modified to include the presence of diluents in syngas. The syngas heating value can be determined from the standard enthalpies of formation of reactant and product species (Turns, 2011). Table 2.3 lists the heating values of various syngas mixtures. For comparison, the heating values of methane (representative of natural gas) on mass and volume basis are 55,500 kJ/kg and 888,000 kJ/kmol, respectively. Thus, the volumetric heat release rate from syngas combustion is low compared to those for methane. There are other such differences between the chemical and physical properties of syngas and natural gas. This presents challenges in replacing natural gas by syngas in existing combustion devices. Table 2.3 also lists the adiabatic flame temperatures (T_{ad}) of various syngas-air mixtures at $\Phi = 1.0$.

The variation of T_{ad} with Φ for different syngas mixtures is plotted in Figure 2.5. The equilibrium temperature (T_{ad}) was computed using the EQUILIBRIUM algorithm in CHEMKIN software (Chemkin, 2007). The algorithm is based on the application of the first and second laws of thermodynamics. As indicated in Figure 2.5, T_{ad} is nearly independent of the CO fraction in syngas. However, diluents, such as CO₂, H₂O, and N₂, can be used to modify its value.

Ignition of a fuel-air mixture is often characterized in terms of ignition delay time (t_{ign}), which has been measured using a variety of devices, including shock tube (Petersen *et al.*, 2007), rapid compression machine (RCM) (Walton *et al.*, 2007) and constant volume (or constant pressure) combustor.

The ignition delay also represents an important target for the development and validation of reaction mechanisms. The computations of t_{ign} are often performed using a homogeneous reactor

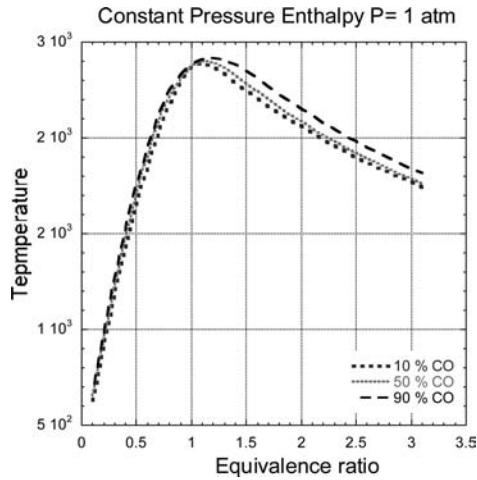


Figure 2.5. Computed adiabatic flame temperature versus equivalence ratio (Φ) for three different syngas mixtures.

model (Aggarwal, 2011). Davis *et al.* (2005), Li *et al.* (2007) and others have reported such mechanisms for syngas oxidation. The GRI-3.0 mechanism (Smith web-link), which includes the oxidation chemistry of C1-C3 species, has also been employed. The homogeneous reactor model is based on the mass and energy conservation equations for a transient, spatially homogeneous system containing a gaseous reacting mixture. Figure 2.6 from Dryer (2008) summarizes the measured and predicted ignition delay data for different syngas mixtures reported by various researchers.

Laminar flame speed or burning velocity represents another fundamental property of a fuel-air mixture. It is of critical importance with regards to flame spread, stabilization, flashback, and blowout in practical systems. In IGCC premixed burners, the problem of flashback and combustion instability represents a major challenge to the designer, especially due to the wide variation in fuel composition. Similarly, it is an important parameter for designing and optimizing the syngas-powered spark ignition (SI) engines, where backfire and inadequate mixing time due to rapid flame propagation represent important issues. The laminar flame speed and its response to stretch are also fundamental to the analysis of premixed turbulent flames. In this context, turbulent flame speed (S_T) is another important property for the combustor design, as it has direct influence on important operational issues, such as flame blow-off, flashback, and combustion instability.

Numerous studies have been reported concerning laminar premixed syngas flames. The primary objective of these studies is to determine the effects of various parameters, such as syngas composition, diluents, temperature, and pressure, on the laminar flame speed, flame stability, and emissions. Laminar burning velocities for H_2 -CO mixtures have been measured using different systems, including flat flame burner (Yan *et al.*, 2011), bunsen burner (Natarajan *et al.*, 2007), counter flow burner (Vagelopoulos *et al.*, 1998), and spherically expanding flames (Prathap *et al.*, 2008). Simulations have often been performed by considering a one-dimensional configuration and employing the PREMIX algorithm (Kee *et al.*, 1993) in CHEMKIN software. Multi-dimensional flame simulations have also been performed using various algorithms (Briones *et al.*, 2008). The computations are based on the solution of mass, momentum, species, and energy conservation equations, along with appropriate models for thermodynamic and transport properties. Such properties include standard enthalpy of formation, viscosity, thermal conductivity, and diffusivity of each species. The number of species depends upon the particular kinetic mechanism employed to model the fuel oxidation chemistry. The above set of equations is closed by using

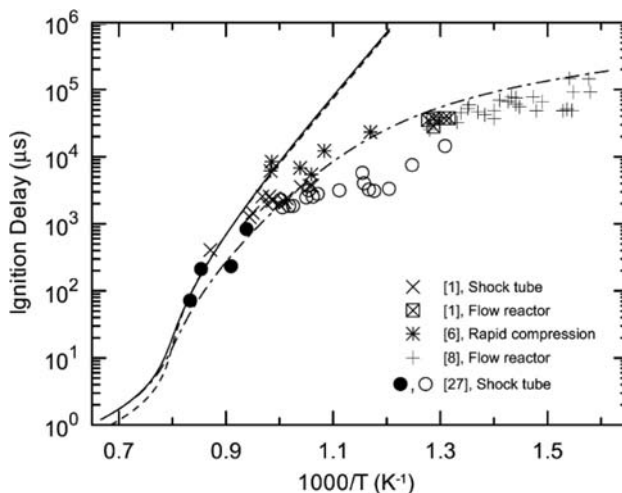


Figure 2.6. Ignition delay times of various syngas and hydrogen mixtures under different pressure and temperature conditions. Filled and open circles correspond to strong and weak ignition events, respectively. All experimental data have been normalized to 20 atm assuming p^{-1} proportionality. Lines correspond to ignition delay predictions using the Li *et al.* mechanism at 20 atm; the solid line corresponds to the syngas mixture used in shock tube experiments (Li *et al.*, 2007).

an appropriate equation of state. The numerical algorithms used for solving these equations have employed different approaches, such as finite-difference and finite-volume schemes. An adaptive grid refining of the computational mesh is often used, based on the first and second derivatives of the dependent variables. Further details can be found in the FLUENT user's guide (2005). Important results from these studies are summarized below:

- Measurements of laminar burning velocity for various syngas-air mixtures have been reported by Mclean *et al.* (1994), Natarajan *et al.* (2009), Kishore *et al.* (2011), and others. Such measurements are often used for the validation of kinetic and thermo-transport models. Figure 2.7 compares the measured and predicted laminar burning velocities for two freely propagating syngas-air flames, corresponding to 50%CO-50%H₂ and 95%CO-5%H₂ mixtures.

Predictions were performed using the PREMIX algorithm in CHEMKIN software. The computational model considers thermal diffusion, multi-component transport, and thermal radiation through an optically thin radiation model. The three models used for syngas oxidation include the Davis *et al.* (2005), GRI 3.0 (2005), and Mueller *et al.* (1999) mechanisms. The comparison in Figure 2.7a indicates that the Davis mechanism is able to reproduce the measured flame speeds for both the mixtures. The effect of syngas composition on laminar flame speed, shown in Figure 2.7b, indicates that the flame speed increases with the increase in H₂ fraction in syngas. This is due to the high diffusivity and reactivity of H₂, since the burning velocity varies as $S_L^2 \sim \sqrt{(D \times \omega_i)}$ (Turns, 2011). In addition, the predicted lean and rich flammability limits for the two cases (Fig. 2.7a) were found to be $\Phi \approx 0.7$ and 5.5, respectively. The flammability limits are expected to be wider with the increase of H₂ fraction in syngas, again due to the high diffusivity and reactivity of H₂. Furthermore, Figure 2.7a indicates that as the amount of H₂ in syngas is increased, the peak in laminar flame speed occurs progressively at higher Φ values. Similar results concerning the effects of equivalence ratio and syngas composition on laminar flame speeds have been reported by others researchers (Som *et al.*, 2008).

- Spherically expanding flames have been commonly used to characterize the flame response to stretch and cellular instabilities. Such phenomena are of fundamental relevance to flame

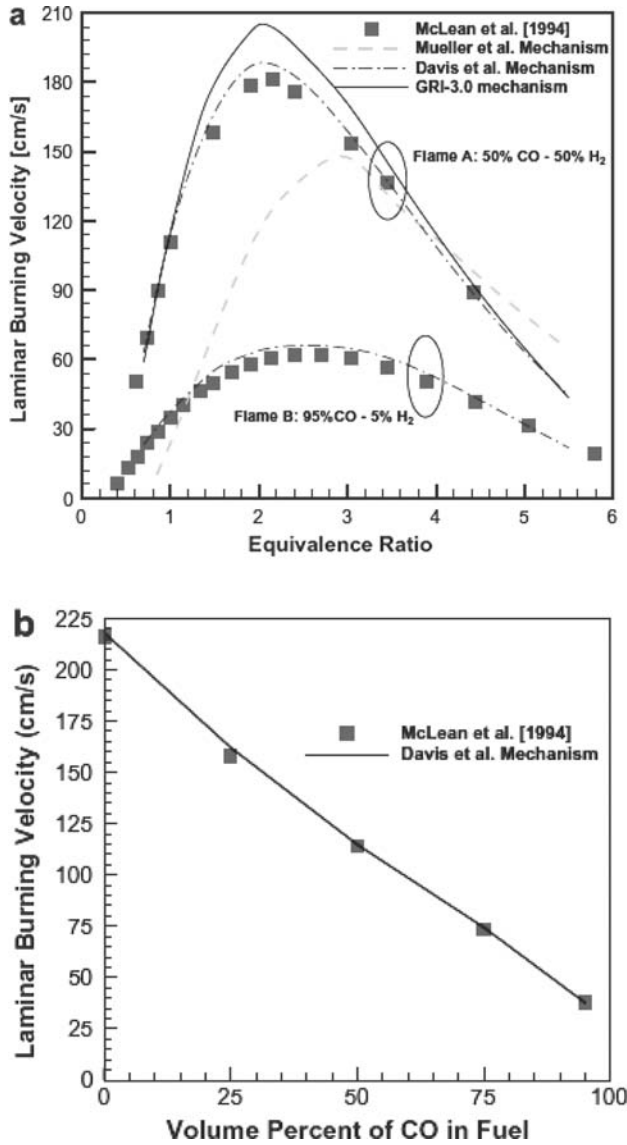


Figure 2.7. Measured and predicted laminar burning velocities for syngas-air mixtures. Variation of laminar flame speed with equivalence ratio Φ for Flames A and B (a), and with CO fraction in syngas at $\Phi = 2.0$ (b) (McLean *et al.*, 1994).

extinction, turbulent flame propagation, flame stabilization, blowout, and transition to detonation. The classical approach yields the following relationship between the stretched flame speed and stretch rate (Mueller *et al.*, 1999):

$$S_L = S_L^\circ - L_a K$$

Here S_L and S_L° are the stretched and unstretched flame speeds, respectively, K the stretch rate, and L_a the Markstein length. Note that S_L° corresponds to the burning velocity of a freely propagating planar flame discussed earlier. The flame stretch refers to the rate of change of

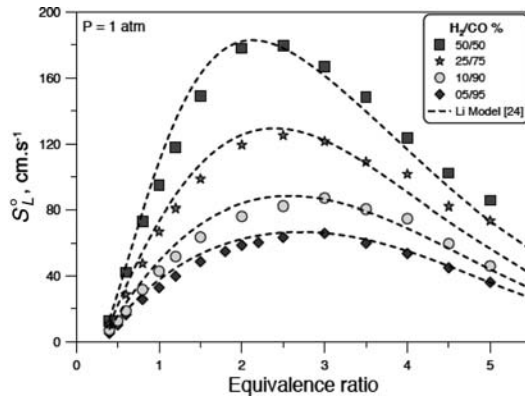


Figure 2.8. Measured and predicted laminar flame speeds for various H_2/CO spherically expanding premixed flames (Bouvet *et al.*, 2011).

the flame surface area, which may be due to flame curvature, unsteadiness, and flow non-uniformity or hydrodynamic stretch (Bouvet *et al.*, 2011). By determining S_L as a function of K through measurements or computations, both S_L^o and L_a can be obtained. Figures 2.7 and 2.8 from Bouvet *et al.* (2011) present such data for spherically expanding H_2/CO flames. Results in Figure 2.7 for the unstretched flame speed are consistent with those presented earlier. The variation of Markstein length with Φ (Fig. 2.8) indicates that these flames are prone to thermo-diffusive instability under lean conditions, since L_a becomes negative for $\Phi < 1$.

As discussed by Kishore *et al.* (2011), this instability is related to the non-unity Lewis number (Le) for stretched flames, with $Le > 1$ and $Le < 1$ corresponding to stable and unstable situations, respectively. Similar behavior has been observed by Pratap *et al.* (2008) and Kishore *et al.* (2011). Further, previous studies have shown that the presence of H_2 in syngas increases the flame propensity for instability, while that of CO has the opposite effect. However, the overall instability is predominantly determined by H_2 rather than by CO .

- Since syngas typically contains significant amounts of CO_2 and H_2O , and N_2 , it is important to examine the effects of these diluents on syngas combustion and emissions. Moreover, dilution is often used to lower the flame temperature and thereby limit NO_x emissions. The effects of various diluents on laminar flame speed and stability have been reported by several researchers (Das *et al.*, 2011; Sun *et al.*, 2007; Law, 2006; Burke *et al.*, 2006; Pratap *et al.*, 2008; Kishore *et al.*, 2011). A general observation is that the addition of these diluents decreases the laminar burning velocity due to the increase in heat capacity and the decrease in heat release rate. For a given amount of dilution, the effect is more pronounced with CO_2 and H_2O dilution compared to that with N_2 dilution, mainly due to different heat capacities. The addition of a diluent also shifts the location of peak laminar burning velocity to leaner mixtures (Kishore *et al.*, 2011). Some studies have also observed that the CO_2 and H_2O addition can affect the combustion chemistry and modify the syngas combustion characteristics (Das *et al.*, 2011). For example, Das *et al.* (2011) observed that the laminar flame speed varies non-monotonically with H_2O addition for CO rich mixtures, but decreases monotonically with H_2O for H_2 -rich mixtures.
- Laminar burning velocity and cellular stability of flames burning other biomass-derived gaseous (BDG) fuels have also been investigated (Burbano *et al.*, 2011). Such studies have considered BDG fuels consisting of varying amounts of H_2 , CO , CH_4 , CO_2 and N_2 . Yan *et al.* (2011) determined unstretched laminar burning velocities for four different BDG mixtures using a perforated flat flame burner. Vu *et al.* (2011) reported laminar burning velocities and Markstein lengths for spherically expanding flames for three different BDG mixtures. The PREMIX 1-D algorithm was used for computing the corresponding burning velocities in these studies.

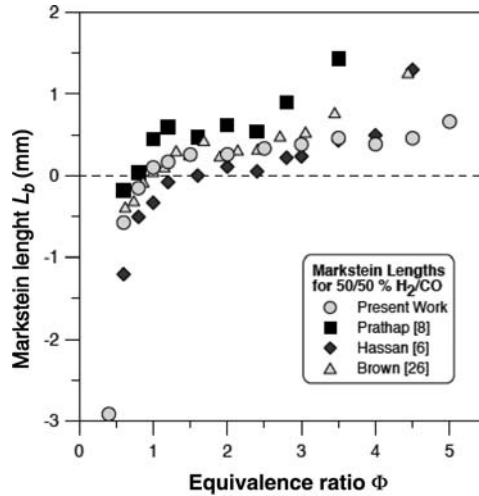


Figure 2.9a. Measured Markstein L_b length versus equivalence ratio Φ for 50/50% H_2/CO spherically expanding premixed flames (Bouvet *et al.*, 2011).

A representative result from Vu *et al.* (2011) is depicted in Figure 2.9a and Figure 2.9b, which plots the unstretched burning velocity versus Φ for three BDG-air mixtures.

As indicated, the revised GRI-3.0 mechanism provides much closer agreement with measurements, especially under rich conditions. In the revised mechanism, rate constants of key reactions were modified based on the data in Davis *et al.* (2005) and Li *et al.* (2007). The Markstein lengths extracted from measurements for the three BDG-air flames were found to be negative, indicating a propensity for cellular instability. In addition, it was observed that the propensity increases and decreases with H_2 and CH_4 addition, respectively, and remains essentially unchanged with CO addition.

- There have been relatively few investigations on emissions from premixed syngas flames, although extensive data have been reported for the hydrocarbon flames. While it is important to consider both soot and NO_x emissions from hydrocarbon flames, only NO_x formation is relevant in syngas flames. NO_x formation in hydrocarbon flames is essentially due to four mechanisms, namely the thermal (Zeldovich), the prompt (Fenimore), N_2O , and NNH mechanisms (Das *et al.*, 2011; Vu *et al.*, 2011; Briones *et al.*, 2007). Thermal NO involves the following reactions: $O + N_2 \Rightarrow N + NO$, and $N + O_2 \Rightarrow NO + O$, and $N + OH \Rightarrow NO + H$. Here the first reaction is the rate limiting step, and becomes significant at high temperatures due to its high activation energy. Prompt NO formation is initiated through the reaction $CH + N_2 \Rightarrow NCN$ (or HCN) + H (or N). Thus the prompt mechanism is absent in syngas flames, since it is directly linked to hydrocarbon combustion chemistry, which produces a CH radical from acetylene. The prompt NO, however, may be important for syngas mixtures containing CH_4 . The N_2O -intermediate mechanism involves $N_2 + O + M \Rightarrow N_2O + M$ as the initiating reaction, with subsequent NO formation occurring through reactions such as $N_2O + H \Rightarrow NO + NH$ and $N_2O + O \Rightarrow NO + NO$. This route is found to become important for lean mixtures and high pressures. Finally, the NO formation through NNH route involves reactions: $N_2 + H \Rightarrow NNH$ and $NNH + O \Rightarrow NO + NH$ (Guo *et al.*, 2007). Ding *et al.* (2011) investigated the extinction and emission behavior of lean premixed syngas flames in a counter-flow configuration. Numerical simulations were performed using the OPPDIF algorithm in CHEMKIN and the Davis Mechanism (Davis, 2005). It was observed that the NO in these flames was formed predominantly through the NNH and N_2O intermediate routes. The contribution of thermal NO was small due to the low flame temperatures. In addition, increasing the CO fraction in syngas was found to increase the amount of NO formed.

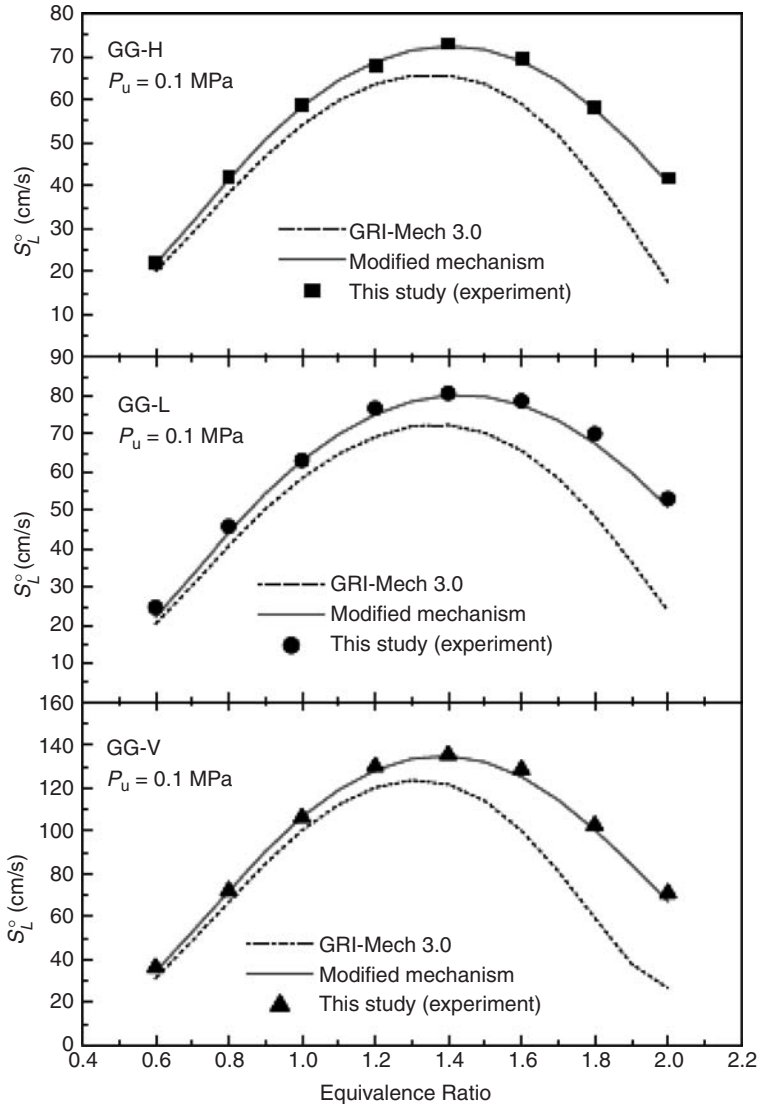


Figure 2.9b. Measured and computed unstretched laminar burning velocities for the three BDG-air pre-mixed flames. Computations are based on the GRI 3.0 (dashed lines), and the revised mechanisms (solid lines) (Vu *et al.*, 2011). P_u : pressure.

2.3.2 Non-premixed and partially premixed syngas flames

Combustion in many practical devices involves non-premixed (diffusion) and partially premixed flames (Bozzeli *et al.*, 1995). While there exist numerous studies of such flames with hydrocarbon fuels, relatively few investigations have appeared with syngas fuels. Giles *et al.* (2006) numerically studied the effects of N_2 , CO_2 , H_2O , and CH_4 addition on the structure and NO_x characteristics of syngas diffusion flames in a counter flow burner. A diffusion flame in this burner is established by having two opposing jets being issued from two coaxial nozzles that are placed one above the other. Fuel is supplied from the bottom jet and air from the top jet, and the flame is established near the stagnation plane formed by the two jets. Diluents can be introduced through either or both the

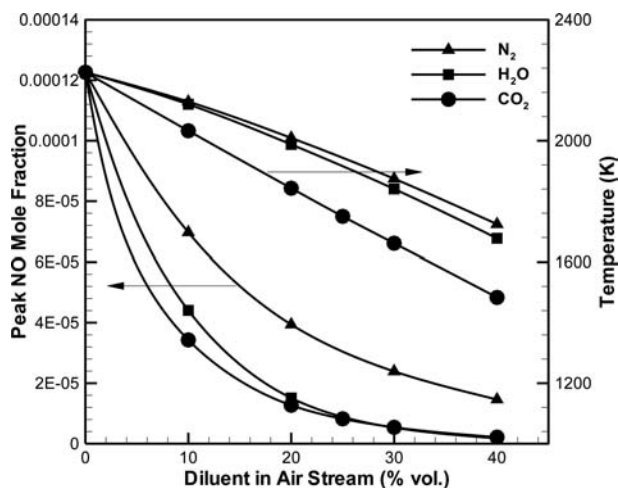


Figure 2.10. Effect of adding N_2 , H_2O , and CO_2 in the airstream on the peak NO mole fraction and flame temperature for a syngas (50% H_2 /50%CO)-air diffusion flame (Giles *et al.*, 2006).

jets. Simulations were performed using the OPPDIF algorithm and the GRI-3.0 mechanism. The algorithm computes the flow field and flame by solving the governing equations for temperature, species mass fraction, and velocity field. The 2-D axisymmetric flow field is transformed into a 1-D problem by employing a similarity transformation. Results indicated that syngas non-premixed flames are characterized by relatively high temperatures and NO_x concentrations, and require diluents to control NO_x emissions. Figure 2.10 from Giles *et al.* (2006) depicts the effects of three diluents (N_2 , H_2O , and CO_2) added to the airstream on the peak flame temperature and NO mole fraction for a 50% H_2 /50%CO syngas flame.

As the amount of dilution is increased, the flame temperature decreases with a corresponding reduction in the peak NO, indicating that NO formation in these flames is primarily due to the thermal mechanism. CO_2 and H_2O are more effective than N_2 in reducing NO, with CO_2 being the most effective diluent on a mole basis. Giles *et al.* (2006) also observed that the presence of methane in syngas even in small amounts opens the prompt NO route, and decreases the diluent effectiveness in reducing NO_x . Other studies on non-premixed syngas flames include those reported by Hui *et al.* (2007) and Park *et al.* (2004).

There have also been few investigations on syngas partially premixed flames (Hui *et al.*, 2007). A partially premixed flame (PPF) in a counter-flow burner is established by introducing air from the top nozzle and a fuel rich mixture from the bottom jet. The important parameters characterizing a counter-flow PPF include the strain rate, equivalence ratio (Φ), and fuel composition. Som *et al.* (2010) investigated experimentally and numerically the influence of pressure and fuel composition on the combustion and NO_x emissions in syngas PPFs. Figure 2.11 from this study depicts images of two PPFs established at $\Phi = 6$ and 16, and strain rate $a_s = 35 \text{ s}^{-1}$. For $\Phi = 6$, which is just above the rich flammability limit of 50% H_2 /50%CO syngas-air mixture, the flame exhibits a typical double flame structure with a weak rich premixed reaction zone (RPZ) established very close to the fuel nozzle and a non-premixed reaction zone (NPZ) on the oxidizer side near the stagnation plane.

As Φ is increased, the RPZ moves away from the fuel nozzle. Consequently, for $\Phi = 16$, the RPZ and NPZ are much closer to each other. The computed structures of four syngas PPFs in terms of the profiles of temperature and heat release rate are shown in Figure 2.12. Two of these flames correspond to the same conditions as those for flames depicted in Figure 2.11. Again, for $\Phi = 6.0$, the flame structure is characterized by two spatially separated reaction zones, namely the RPZ

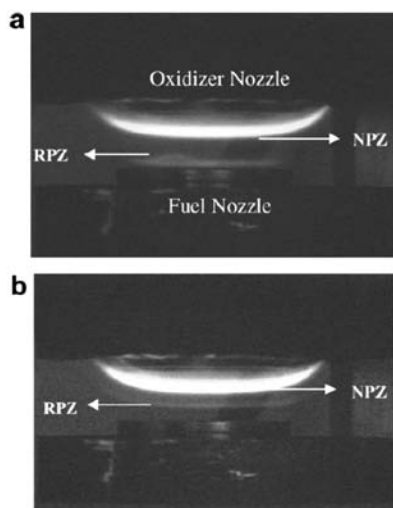


Figure 2.11. Images of syngas (50% H_2 /50% CO)-air partially premixed flames established at $\Phi = 6$ (Flame a) and $\Phi = 16$ (Flame b) in a counter flow burner. The strain rate is 35 s^{-1} (Som *et al.*, 2010).

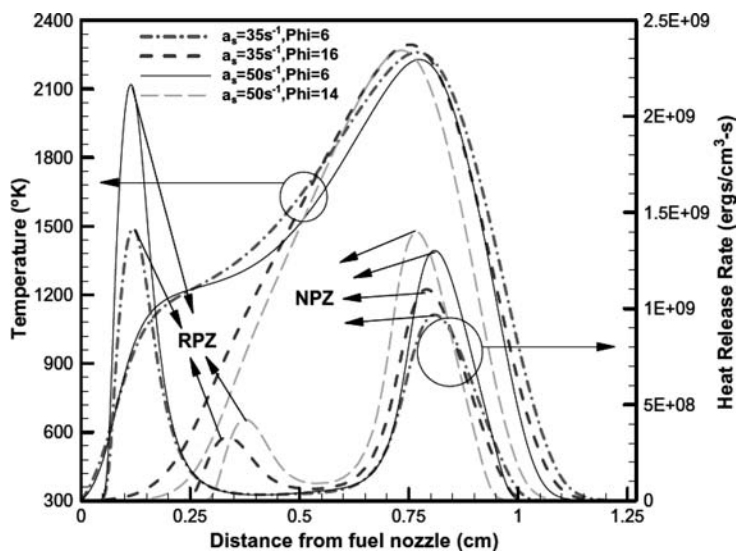


Figure 2.12. Computed flame structure in terms of temperature and heat release rate profiles for four syngas (50% H_2 /50% CO)-air partially premixed flames. The two flames at strain rate $a_s = 35 \text{ s}^{-1}$ are the same as those depicted in Figure 2.13, while the other two flames are at $a_s = 50 \text{ s}^{-1}$ and $\Phi = 6$ and 16.

and NPZ, which are easily located by the two heat release rate peaks. The RPZ is very close to the fuel nozzle, which is in agreement with the digital images presented in Figure 2.11. For $\Phi = 16$, the temperature peaks indicate a nearly merged flame structure. However, the corresponding heat release rate profiles indicate two distinct peaks that are close to each other. This is again consistent with the digital images in Figure 2.11. At lower strain rates ($a_s = 35 \text{ s}^{-1}$), flame temperatures are slightly higher due to longer residence time.

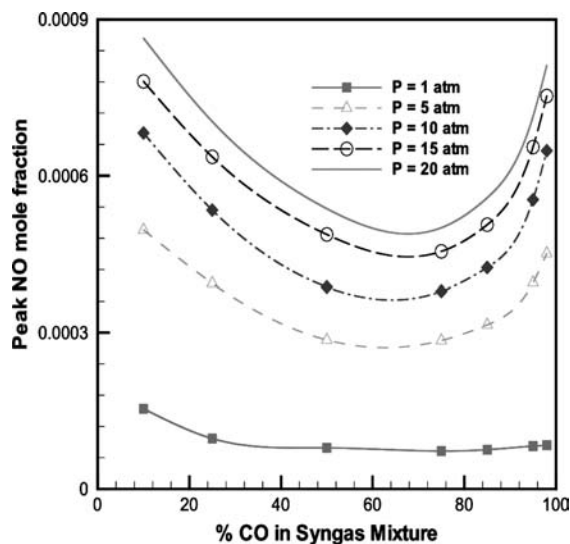


Figure 2.13. Peak NO mole fraction plotted versus CO fraction in syngas for partially premixed flames established at $\Phi = 6$ and different pressures (Som *et al.*, 2010).

Som *et al.* (2010) further observed that for the conditions investigated, the RPZ is characterized by H_2 oxidation, while the NPZ is characterized by the oxidation of both H_2 and CO. This is in contrast to hydrocarbon PPFs, in which the fuel is partially oxidized to produce H_2 and CO in the RPZ, and the oxidation of H_2 and CO occurs in the NPZ. However, similar to hydrocarbon PPFs, as the pressure is increased, the distance between the two reaction zones decreases, while the flame temperature increases. The reader is referred to Figure 8 in Som *et al.* (2010) for further discussion of the flame structure at different pressures and syngas compositions. With regards to NO emission, results indicated that as the pressure is increased, the amount of NO formed first increases rapidly with pressure, but then levels off at higher pressures. This can mainly be attributed to the increase in flame temperature with pressure, which increases the thermal NO. In addition, the peak NO exhibits a non-monotonic variation with the H_2 fraction in syngas, as shown in Figure 2.13. As the H_2 fraction is increased, the peak NO first decreases and then increases. This can be attributed to the combined effects of thermal and re-burn mechanisms, as the syngas composition is changed.

The re-burn mechanism consumes NO through reactions $NO + H + M \Rightarrow HNO + M$ and $NO + O + M \Rightarrow NO_2 + M$, which become important at higher pressures and as the H_2 fraction in syngas increases. However, when the H_2 fraction exceeds a certain value, the peak NO starts increasing with the increase in H_2 fraction, which is due to the effect of higher flame temperature, which increases thermal NO. The contributions of various NO formation routes are depicted in Figure 2.14 from Som *et al.* (2010) which plots the NO emission index with respect to pressure for two different syngas mixtures. The emission index is defined as the ratio of NO production rate to fuel consumption rate. As indicated in the figure, the N_2H , NNH, and re-burn mechanisms become important at high pressures.

Ouimette and Seers (2009) reported an experimental investigation on syngas partially premixed jet flames. The effects of Φ , CO_2 dilution, and H_2/CO ratio on the flame structure and NO_x were reported. Figure 2.15 from this reference presents images of syngas jet flames at different Φ . As expected, the flame length is strongly influenced by the level of partial premixing.

As Φ decreases from the non-premixed to premixed regime, the flame length decreases monotonically. This has important consequences for the emissions of NO_x , greenhouse gases, and

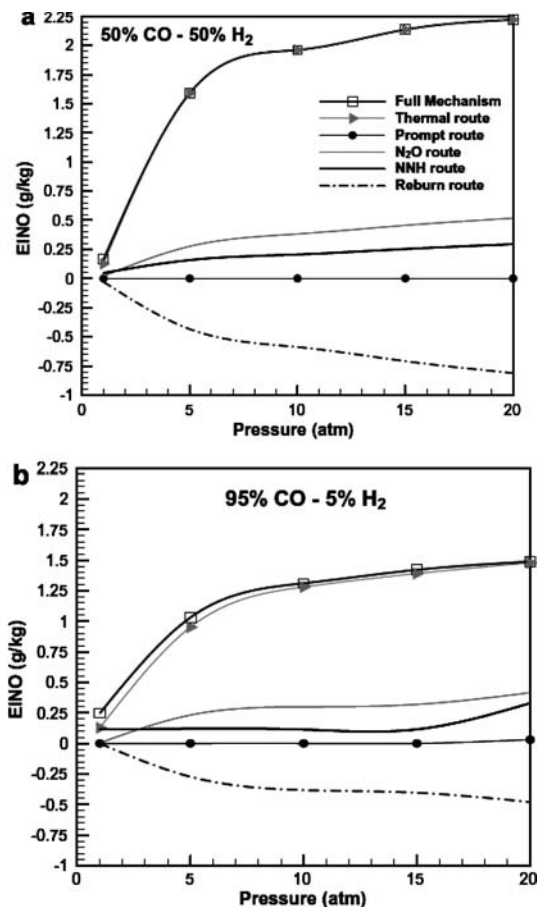


Figure 2.14. Variation of emission indices of total, thermal, prompt, N_2O , NNH and reburn NO mechanisms with pressure for syngas partially premixed flames (Som *et al.*, 2010).

other pollutants, since the flame length directly influences the reacting volume and residence time. In addition, images at 2.0 and 1.6 indicate the existence of two reaction zones, with the NPZ enveloping the RZP. Regarding NO_x , results indicated that EINO_x first increases as Φ is increased from 1.0 to 1.6, then remains nearly constant for $1.6 < \Phi < 3.85$, and subsequently decreases slowly as Φ is increased to the diffusion limit ($\Phi \Rightarrow \infty$). In addition, results indicated that increasing CO_2 dilution reduces EINO_x in the entire range of Φ , consistent with previous studies while increasing the H_2/CO ratio reduces EINO_x for $\Phi < 2.0$, and has negligible effect for richer mixtures.

2.3.3 High pressure and turbulent syngas flames

There has been relatively little work concerning high pressure syngas flames. McLean *et al.* (1994) and Vagelopoulos and Egolfopoulos (1998) reported premixed flame speeds at pressures from atmospheric to a few atmospheres. Burke *et al.* (2007) examined the effect of CO_2 on burning velocity of spherically expanding flames at $p = 1.0$ and 10 atm using a 25% H_2 -75% CO mixture with 12.5% O_2 -87.5% He oxidizer. Sun *et al.* (2005) reported laminar flame speeds for

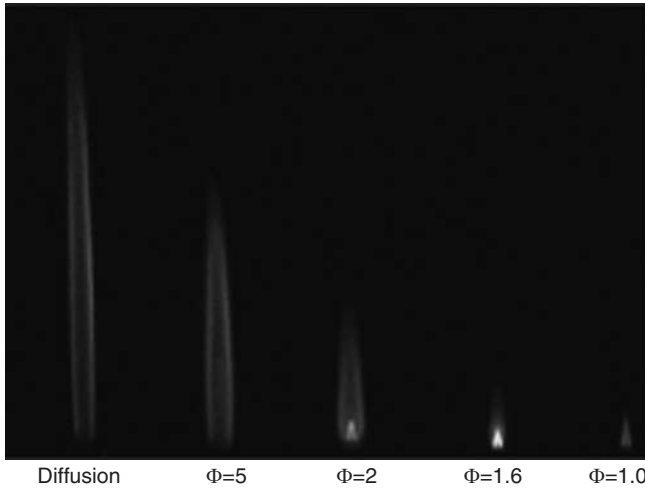


Figure 2.15. Images of laminar partially premixed 45% H_2 /35% CO /20% CO_2 –air flames at different levels of partial premixing and Reynolds number of 1400 (Ouimette and Seers, 2009).

$\text{CO}/\text{H}_2/\text{air}$ and $\text{CO}/\text{H}_2/\text{O}_2/\text{He}$ mixtures for pressures up to 40 atmospheres using the constant-pressure spherical flame technique. A kinetic model was also developed using the latest available thermo-transport and kinetic data (Park *et al.*, 2004; Ouimette, 2009). The mechanism was validated against the measured flame speeds, non-premixed counter flow ignition temperatures, concentration profiles in a flow reactor, and ignition data from shock tube experiments. Figure 2.16 from their study shows the measured and predicted laminar flame speeds plotted *versus* Φ for $\text{CO}/\text{H}_2/\text{O}_2/\text{He}$ mixtures at different CO/H_2 ratios, and pressures of 5–40 atm.

Predictions are based on their kinetic model and that reported by Davis *et al.* (2005). As expected, the flame speed increases with increasing H_2 content, and decreases with increasing pressure. Overall, there is good agreement between the predictions and measurements, although both models exhibit discrepancies, which may be attributed to uncertainties in kinetic and transport data. Thus, further studies are warranted for high-pressure syngas flames over a range of combustion regimes, including non-premixed and partially premixed combustion, and using different burners.

Studies on turbulent syngas flames have focused on the determination of turbulent flame speeds (S_T) (Chase *et al.*, 1951; Kee *et al.*, 1995; Daniele, 2011). While S_T can be defined in multiple ways, it is often based on a global consumption speed (Venkateswaran *et al.*, 2011) and is presented in terms of the normalized flame speed (S_T/S_L) as a function of turbulence intensity, fuel composition and other parameters. Daniele *et al.* (2011) considered the reaction zones regime and examined the effects of pressure and syngas composition on the turbulent flame speed. Correlations were developed for S_T/S_L as a function of normalized parameters representing the effects of turbulence intensity, integral length scale, pressure, and temperature.

The increase of S_T/S_L with increasing pressure and H_2 content was attributed to the thermo-diffusive and hydrodynamic instabilities. Venkateswaran *et al.* (2011) reported measurements of global turbulent flame speeds using a Bunsen burner, and examined the effects of Φ , syngas composition, mean flow velocity, and turbulence intensity. Consistent with other studies, the flame speed was found to exhibit sensitivity to fuel composition over a wide range of turbulence intensity, increasing significantly with the increase in H_2 content. The data were further analyzed to develop flame speed correlations, indicating the effects of thermo-diffusive instabilities through negative Markstein lengths.

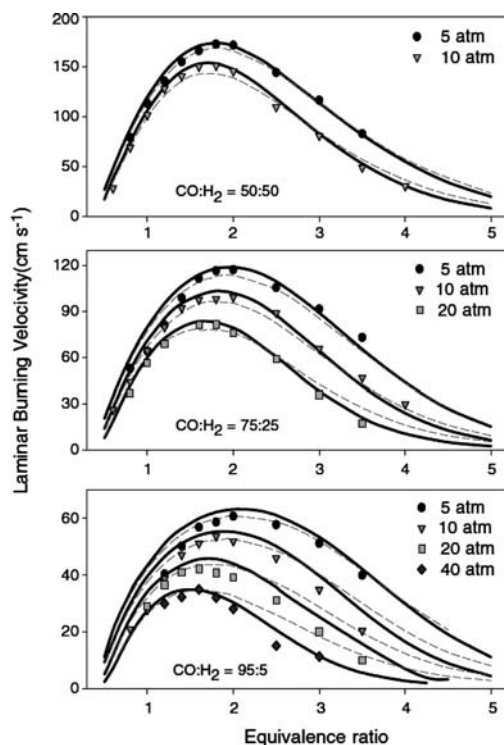


Figure 2.16. Measured and predicted laminar flame speeds versus Φ for different CO/H₂/He/O₂ mixtures at 5, 10, 20, and 40 atm. Predictions are based on the kinetic models of Sun *et al.* (2005) (solid line) and Davis *et al.* (2005) (dashed line).

2.3.4 Syngas combustion in practical devices

Syngas combustion in gas turbine engines (i) using an IGCC facility is quite promising for efficient, low-emission power generation, and for carbon capture and storage. Research in this area has focused on using syngas in natural gas-fired combustors (Monteiro, 2011). Similarly, some studies (Luessen, 1997; Colantoni *et al.*, 2010; Boehman *et al.*, 2008) have demonstrated the viability of using syngas in spark ignition (SI) and compression ignition (CI) engines. Sahoo *et al.* (2011) examined the effects of using syngas on the performance and emission characteristics in a diesel engine operating in a dual-fuel mode, using a combination of diesel pilot injection and syngas fumigation in the intake air (Boeman *et al.*, 2008). In this mode, the ignition is initiated through the auto ignition of diesel fuel. Results indicated that the engine performance and emissions are strongly influenced by the syngas composition, depending upon the load and other conditions. In general, increasing the H₂ fraction in syngas was found to improve engine performance, reduce CO and hydrocarbon emissions, but increase NO_x emissions. Thus, further experiments and simulations are needed to optimize the engine performance and emissions for various operating conditions and syngas composition. Research should also focus on examining the use of syngas in new engine designs, such as HCCI (Homogeneous Charge Compression Ignition) and low temperature combustion.

The use of syngas in SI engines also offers advantages, such as better anti-knocking properties and operation with leaner mixtures. Improved knock resistance is due to the presence of CO and CH₄, and enables operation at a higher compression ratio, leading to higher thermal efficiency. However, a higher burning rate due to the presence of H₂ can result in higher end gas temperature and increased propensity to knocking. The presence of H₂ can also increase

Table 2.4. Representative biogas compositions based on two common feed stocks.

Chemical species	Biogas 1 Agricultural waste	Biogas 2 Household waste
CH ₄	68%	60%
CO ₂	26%	33%
H ₂ O	5%	6%
N ₂	1%	1%
O ₂	0%	0%

NO_x emissions, which may be controlled by using leaner mixtures (Boeman *et al.*, 2008). Bika *et al.* (2011) examined such issues by performing single cylinder experiments for different syngas compositions, compression ratios, and equivalence ratios. For a given Φ and spark timing, the knock limited compression ratio was observed to increase with increasing CO fraction. The burn duration and ignition lag also increased with increasing CO fraction.

2.4 BIOGAS COMBUSTION AND EMISSIONS

Biogas or landfill gas (LFG) is typically produced from anaerobic decomposition of organic matter in an oxygen-free environment (Saho *et al.*, 2011). It can also be produced through pyrolysis and gasification processes. Primary sources include biomass, green waste, plant material, manure, sewage, municipal waste and energy crops. While its composition can vary significantly depending on the source and production process, the main constituents include CH₄ (50–75% by volume), CO₂ (25–40%), N₂ (0–10%), and small traces of H₂O, O₂, H₂, and hydrogen sulfide. It may also contain small amounts of contaminants such as volatile organic compounds, sulfur compounds, siloxanes, halogenated hydrocarbons, ammonia, etc. To account for this variation in composition, previous studies have examined the biogas combustion and emission behavior for some specific compositions. Table 2.4 lists two such representative biogas mixtures based on the two common biomass sources, namely agricultural waste and household waste (Bika *et al.*, 2011). Like natural gas and syngas, biogas can be used as a transportation fuel in IC engines, and for power generation in gas turbines and boilers. It can also be used as compressed natural gas, and in solid oxide fuel cells to generate electricity. Moreover, it can be reformed to produce syngas and then used in the above applications.

There is a large body of literature on methane combustion, including ignition, extinction, flammability limits, flame speeds, cellular instabilities, and emissions. Consequently, detailed thermo-transport and kinetic models have been developed to simulate and analyze methane flames in a variety of configurations. Considerable research has also been reported on fire suppression, which has examined the extinction and blowout of methane–air flames using various diluents, such as CO₂, N₂, H₂O, and chemicals (Gunaseelan, 1997; Quesito, 2011). Most of these studies and the associated models can be readily used for analyzing the combustion and emission characteristics of biogas, whose main constituents are CH₄ and CO₂ with small traces of H₂O, and N₂. This section provides a brief overview of the fundamental combustion properties of biogas, and its application in IC engines. For more detailed discussion, the reader is referred to the extensive literature available on methane combustion and emissions.

Biogas has lower energy content compared to natural gas. For example, the volumetric heating values of natural gas (94% CH₄) and biogas (60%CH₄/40%CO₂) are 38.6 and 25 MJ/m³, respectively. This has consequences for using biogas in natural gas-fired combustion devices, since the lower heating value implies higher feeding rates and lower flame temperatures. Figure 2.17 compares the predicted adiabatic flame temperatures for methane-air and two biogas-air mixtures, shown in Table 2.4.

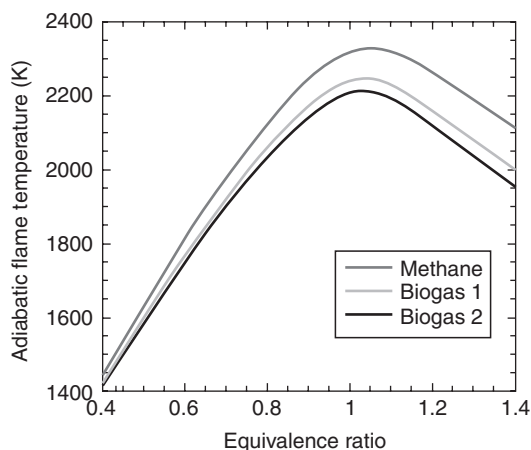


Figure 2.17. Comparison of adiabatic flame temperatures of methane-air and two biogas-air mixtures. The biogas compositions are given in Table 2.4. Pressure is 1 atm, and initial temperature 500 K.

As indicated, the biogas flame temperature is about 100–200 K lower than that of methane. Lower temperatures imply lower flame speeds and thermal NO for biogas flames compared to those for methane flames. The comparison of laminar burning rates for freely propagating methane and biogas flames is shown in Figure 2.18, which plots the flame speed as a function of equivalence ratio and pressure. The flames were computed using the PREMIX algorithm in CHEMKIN software along with the GRI-3.0 kinetic mechanism. As expected, results indicate lower flame speeds for biogas-air mixtures compared to those for methane-air mixtures. The effect of pressure on flame speed is qualitatively similar for all three cases shown, with the flame speed first decreasing sharply and then relatively slowly as the pressure is increased.

Since biogas is potentially a cleaner and more sustainable alternative to natural gas, it is relevant to analyze methane and biogas flames over different combustion regimes. Figure 2.19 from Aggarwal (2009) depicts the computed structures of methane-air and biogas-air partially premixed flames in terms of temperature, velocity, and species mole fraction profiles.

The counter flow flames were established at $\Phi = 1.4$, pressure = 1 atm, and strain rate = 200 s^{-1} , using the OPPDIF algorithm and GRI-3.0 mechanism, as stated earlier. For all three cases, the flames exhibit a double flame structure with a rich premixed reaction zone (RPZ) located on the fuel side and a non-premixed reaction zone (NPZ) on the oxidizer side near the stagnation plane, which is located by the zero value of the axial velocity. The fuel is completely consumed in the RPZ, producing CO, H_2 , and intermediate hydrocarbons, which are transported to and consumed in the NPZ. The two reaction zones can also be located by the two local peaks in axial velocity profiles (Fig. 2.19), and by the peaks of CO and CO_2 mole fractions, respectively. For example, the RPZs for the three flames are located at 0.85, 0.9, and 0.91 cm, respectively, from the fuel nozzle, based on the peak CO locations, while the NPZ are located at 0.975, 0.963, and 0.95, respectively, based on the peak CO_2 locations. The NO profiles indicate a significantly lower level of NO formation in biogas PPFs compared to that in methane PPFs. This may be attributed to the less thermal NO and prompt NO formed, indicated by lower temperatures and C_2H_2 peaks, in biogas flames compared to those in methane flames.

Like syngas, there are relatively few studies on the performance and emission behavior of biogas-fed combustion devices. Henham and Makkar (1998) and Yoon and Lee (2011) reported experimental investigation on the combustion and emission characteristics of dual-fuel CI engines using diesel and biogas. These studies were able to point out the viability of dual-fuel engines for using fuels with low energy content like biogas. Bedoya *et al.* (2011) performed an experimental

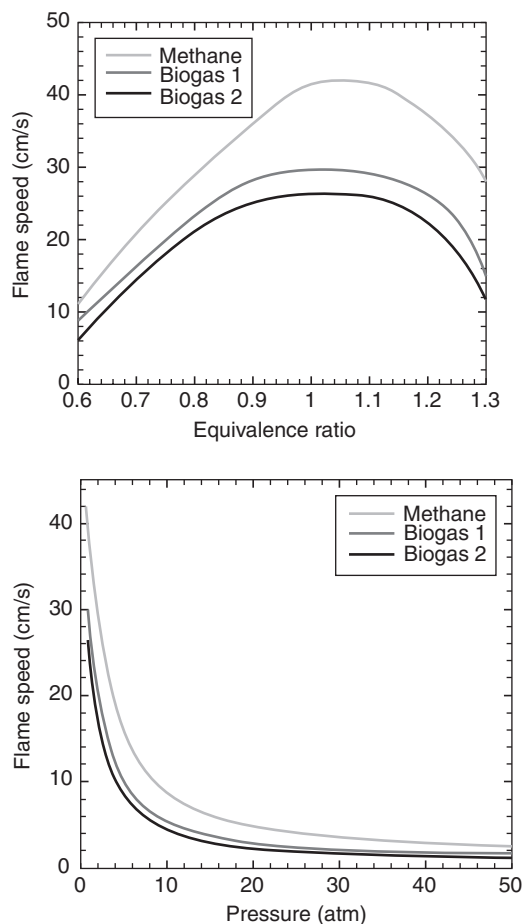


Figure 2.18. Comparison of laminar flame speeds of methane-air and two biogas-air mixtures. Flame speed is plotted *versus* equivalence ratio (top) and pressure.

study of biogas combustion in an HCCI engine for high efficiency and ultra-low NO_x emissions. Kohn *et al.* (2011) performed experiments on a SI engine operating on LFG and syngas. The syngas addition was found to improve the engine efficiency and reduce emissions of CO, UHC, and NO_x .

2.5 CONCLUDING REMARKS

Biomass pyrolysis and gasification processes have been sufficiently developed to play a significant role in our sustainable energy future, especially as part of a biorefinery. While these processes can yield a number of gaseous and liquid fuels, this chapter provides a review of studies on the combustion and emission characteristics of syngas and biogas. There are notable differences between the combustion behavior of these two fuels and that of hydrocarbon fuels. While the syngas composition can vary widely, it generally has lower heating value, higher flame speeds, wider flammability limits, lower density, and higher mass diffusivity. Similarly biogas has lower heating value compared to natural gas, and significant variation in its composition. Such differences imply different optimum operating conditions for combustion devices using these fuels, and thus significant opportunities for fundamental and applied research on both the production and utilization of such fuels. Fundamental combustion aspects requiring further research include

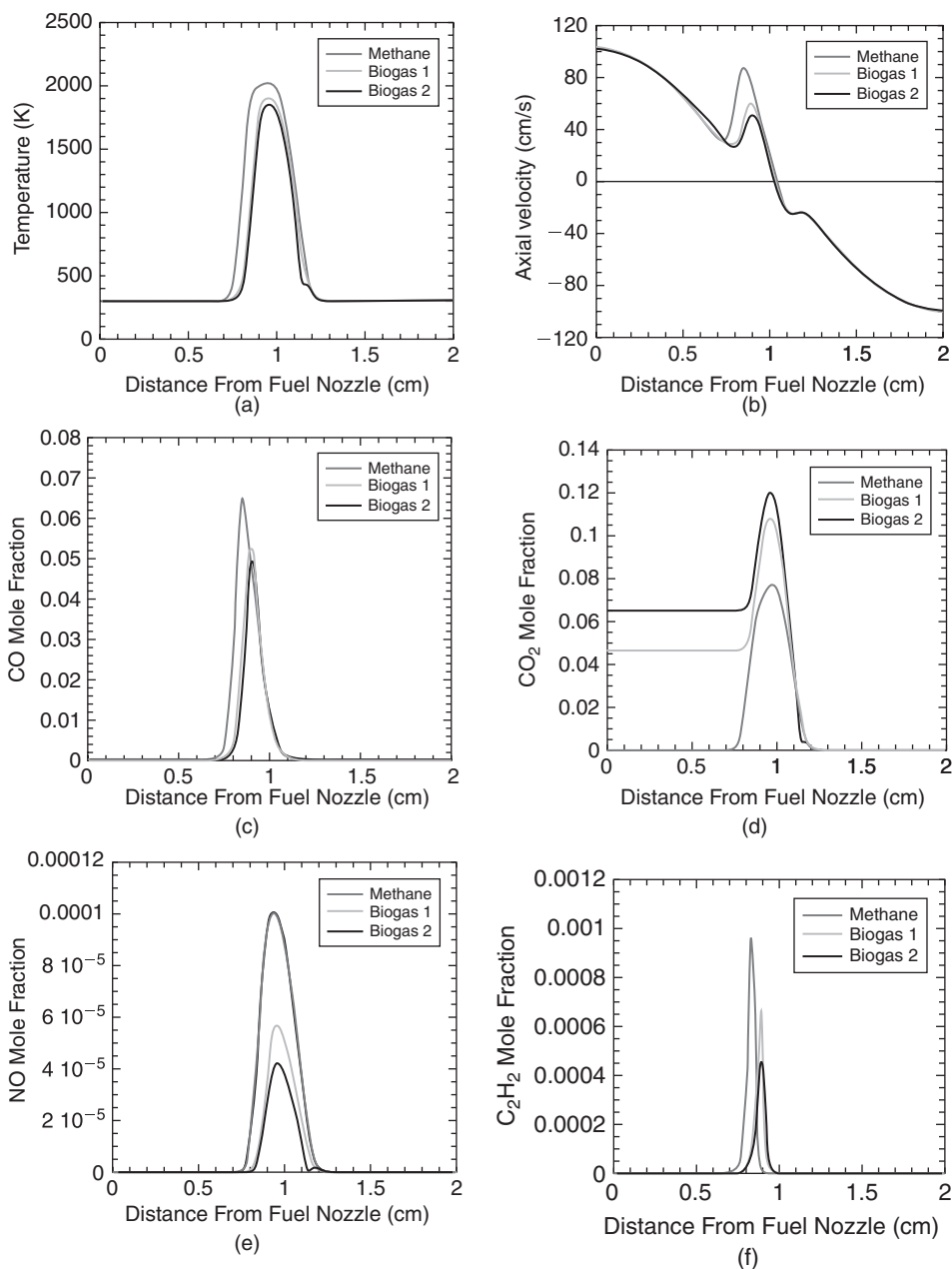


Figure 2.19. Flame structures in temperature, velocity, and species profiles for methane-air and biogas-air partially premixed flames at $\Phi = 1.4$, pressure = 1 atm, and strain rate = 200 s^{-1} .

cellular instabilities, flame stabilization and blowout behavior, turbulent flames, and emission characteristics. Such efforts would lead to the development of optimized systems for producing these fuels, and provide general guidelines for optimizing their composition for a given set of operating conditions.

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CHAPTER 3

Energy conversion through combustion of biomass including animal waste

Kalyan Annamalai, Siva Sankar Thanapal, Ben Lawrence, Wei Chen, Aubrey Spear & John Sweeten

3.1 INTRODUCTION

Coal in the power generation industry is the norm since it represents a steady supply *in lieu* of the vast reserves in the USA and it is the cheapest available fossil fuel. According to the US Energy Information Administration (EIA), coal accounts for 43.1% of the total energy consumed for power generation. In the year 2010 coal consumption in the power sector was to the tune of 1085.3 million short tons, which is around 92% of the total coal consumption in the USA (Watson *et al.*, 2011).

The combustion of fossil fuels particularly coal, a solid fuel, poses many challenges due to the pollution it creates. Coal combustion releases carbon dioxide (CO_2) of about 90 kg/GJ, which aids in the phenomena of global warming. The US Environmental Protection Agency (EPA) reports that nitrogen oxides are one of the major pollutants generated in the USA and a large fraction of it comes from coal-fired power plants. As opposed to fossil fuels, the biomass fuels are CO_2 neutral. Thus, extensive research is being conducted to reduce CO_2 emission by using renewable fuels such as wind, solar, agricultural biomass fuels (AgB) and hydrogen generated from fossil fuels and splitting water into hydrogen (H_2) and oxygen (O_2).

Figure 3.1 shows a comparison between AgB energy and hydrogen energy cycles. In the biomass cycle, photosynthesis is used by autotrophs (photosynthesizing organisms, Fig. 3.2) to split CO_2 into carbon (C), O_2 , and water (H_2O) into H_2 , O_2 , produce hydrocarbon (HC) fuel (e.g. leaf) and release O_2 . The O_2 released is used back to combust HC and produce the CO_2 and H_2O , which are returned to produce wood and AgB and release O_2 . On the other hand, in the hydrogen cycle

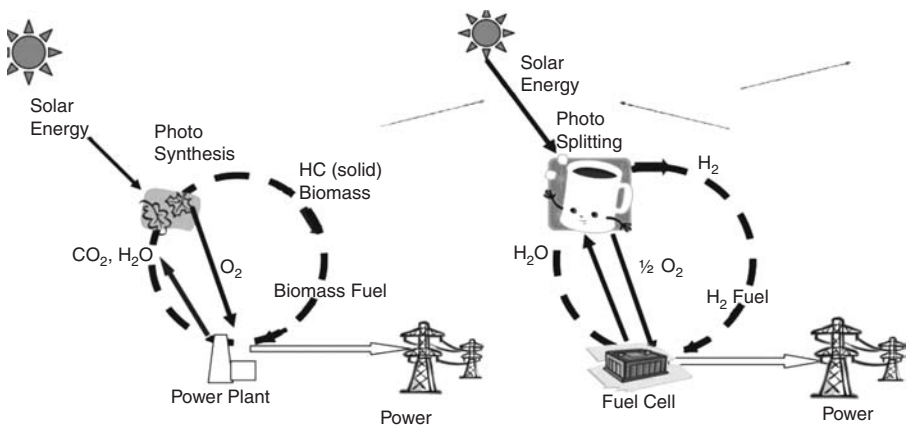


Figure 3.1. Comparison between biomass energy and hydrogen energy cycles, adopted from (Annamalai *et al.*, 2007b).

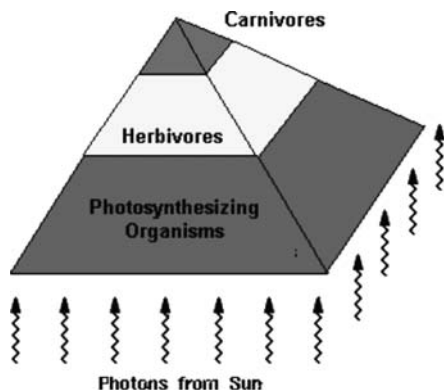


Figure 3.2. The Pyramid of Life; The base of this pyramid is occupied by organisms called autotrophs which are utilizing photosynthesis for extraction of energy and negative entropy from the sun's radiation. Other organisms (herbivores and carnivores) are utilizing energy and negative entropy stored in food, during the process of digestion. (Mieszkowski *et al.*, 1992).

H₂O is dissociated using the photo-splitting process to produce H₂ and O₂, and then use H₂ and O₂ for the combustion process. Photosynthesis is water intensive; most of the water supplied to plants evaporates through leaves and is highly inefficient for conversion to electrical power.

The AgB is consumed by herbivores and processed into solid waste called manure or animal waste based biomass (AnB) as a byproduct of digestion and this biomass is almost a chemical replica of foods they consumed. As a matter of fact, Sweeten *et al.* (2003) had shown that the dry ash-free (DAF) gross or higher heat value (HHV) of cattle manure or cattle biomass (CB) is almost the same as the DAF HHV of agricultural ration fed to the cattle. The heat values of CB are comparable to low quality TX lignite coal.

This chapter gives an overview on energy conversion from animal wastes, fuel properties and TGA analyses, and various thermal energy conversion processes including co-firing, reburn and gasification.

3.2 OVERVIEW ON ENERGY CONVERSION FROM ANIMAL WASTES

3.2.1 Manure source

Managing the amount of manure produced from the hundreds, sometimes thousands, of animals on the farm which house dairy cows, beef cattle, hogs, chickens, and other traditional farm animals, is a significant undertaking (Centner, 2004). In the US, 33.7 million head of cattle were slaughtered in 2006. Kansas and Nebraska were the first and second largest producers of commercial cattle, respectively, with each producing over seven million cattle. Texas was the third largest producer of commercial cattle with 6.48 million head (NASS, 2007).

The potential manure production from cattle in feedlots is over 365 million wet tonnes per year for the US; 70.4 million wet tonnes per year for Texas. Most of these cattle are kept in highly concentrated feedlot operations during the weeks before they are slaughtered. Potentially harvestable manure biomass from all of the concentrated animal feeding operations (CAFOs) in the US easily exceeds 100 million dry tonnes per year and 6–12 million dry tonnes in the Texas Panhandle alone. Sometimes it is cheaper to store them and spread it over the land. Feedlots in the Texas and Oklahoma panhandle regions can range between 5000 and 75,000 head (Harman, 2004). The Texas Panhandle is regarded as the "Cattle Feeding Capital of the World", producing 42% of the fed beef cattle in the United States within a 200-mile radius of Amarillo. Manure produced from the 7.2 million head fed each year amounts to more than 5 million tonnes/year

on an as-collected basis. Hence, it has been used extensively for irrigated and dry land crop production, and in some cases on CRP lands being converted to rangelands. Declining water tables in the Ogallala Aquifer and increasing fuel costs have reduced irrigation water use per acre. As these trends continue, they will likely reduce demand for manure as fertilizer in a per-acre basis. Cattle feedlots will encounter longer hauling distances to achieve P- or N-based nutrient balances on irrigated crops or dry land situations. The amount of manure to be applied is usually determined by the amount of nitrogen contained in the solids. One hectare of grass requires about 250 kg of N. Sometimes this can lead to an overloading of phosphorus on the land. Only recently have farms begun to switch to P-based land application and composting (Osei *et al.*, 2000).

Apart from cattle feedlots, the number of dairy operations with more than 500 head of cows increased from 29% of all dairies in 1997 to 39% of all dairies in 2001. Even though the overall number of dairy operations in the US has declined to 91,240 in 2002, 86,360 in 2003, and 81,440 in 2004, the expansion in milk output is well established and should continue with only modest deceleration (USDA, 2005). This is because the number of larger, more efficient dairies, with over 500 head of cows, has increased while smaller dairies have begun to disappear (Keplinger *et al.*, 2004; NASS, 2002). Among dairy cattle, feeder steers or heifers, each animal (having a live weight between 544 to 907 kg/head or 1200 and 2000 lb/head) produces between 27 to 57 kg (approximately 5 to 6% of its body weight) of wet manure per day containing 85–90% moisture and 10–15% solids (including volatile matter, nutrients, ash and combustibles; Fig. 3.3) (DPI&F, 2003). About 110,000 dairy cattle in over 250 dairies in Erath County produce 1.8 million tonnes of manure biomass (excreted plus bedding) per year. The dairy cows in this region make up about 25% of the total number of dairy cows in Texas (TX PEER, 1998). Dairy manure termed as dairy biomass (DB) is used over 7% of the landscape in the Bosque River Watershed.

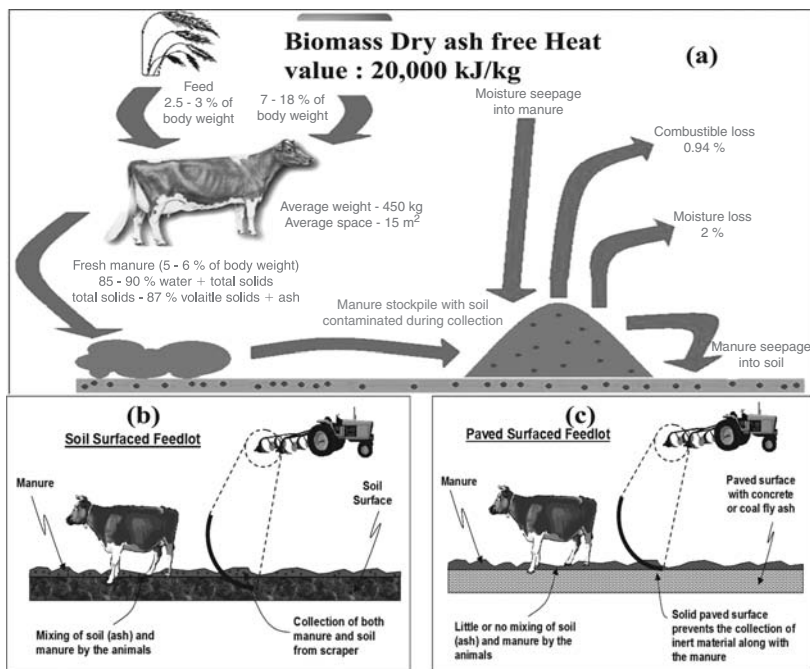


Figure 3.3. (a) Manure production and environmental effects, (b) soil surfaced feedlot manure or high ash feedlot biomass or HAFB (Carlin, 2009), (c) paved surfaced feedlot manure or low ash (LA) feedlot biomass or LAFB; (Carlin, 2009).

Currently most dairies, as well as other CAFO's, utilize large lagoon areas to store wet animal biomass. Water along with nutrients seeps into the soil (Fig. 3.3). This has been the case, for example, in the Bosque River Region and Erath County, just north of Waco, Texas. Water runoff from these lagoons has been held responsible for the increased concentration of phosphorus and other contaminants in the Bosque River, which drains into Lake Waco, the primary source of potable water for Waco's 108,500 people. Thus the growth of cattle, dairy and swine industries will likely exacerbate the nutrient balance situation (Annamalai *et al.*, 2012). Further, when the manure gets very dry, the cattle's feet grind the dry manure, creating a dust problem. Particulate matter (PM) or dust from feedlot ranges from 8.5 to 12 microns. The total suspended particles (TSP) in feedlot dust normally range from $150 \mu\text{g}/\text{m}^3$ to $400 \mu\text{g}/\text{m}^3$ but there are also reports having average values exceeding $400 \mu\text{g}/\text{m}^3$ (Sweeten *et al.*, 1979). The PM 10 regulation requires concentration of particles less than $10 \mu\text{m}$ should be less than $150 \mu\text{g}/\text{m}^3$. Moreover, when wet and composting manure streams decompose or anaerobically digest in relatively uncontrolled settings, such as poorly maintained manure storage lagoons, methane (CH_4) and malodorous odors can form, reducing the quality of life near the farm (Mukhtar, 1999). A video demonstration on biogas from a digester is available at the web site Climatetechwiki (2010). Methane is also a very strong (about 24 times more harmful than CO_2) greenhouse gas.

The total energy usage ranged from as low as 464 kWh per year per head (kWh/y/hd) for a pasture dairy in Northeast Texas, to as high as 1637 kWh/y/hd for a hybrid facility in Central Texas. Where possible, the electricity usage at the dairies was allocated to four main energy sinks: the milking parlor, the animal housing areas, feeding, and manure management. Generally, milking and housing components dominated the electricity usage for hybrid dairies, with the milking parlor being the primary consumer of energy for the open-lot facilities (Sweeten *et al.*, 2012).

The total amount of agricultural manure in the 15 EU countries was estimated to be 1124×10^6 tonnes in 1993 which includes 887×10^6 tonnes from cattle (Eurostat, Waste Statistics). The total energy consumption of the 27 EU member countries in 2009 was 1,113.6 million tonnes of oil equivalent, the biomass consumption made up 7.5% with 83.68 Mtoe. 43.9 Mtoe was input to power plants. Figure 3.4 summarizes the contribution every biomass category can make to the total EU biomass potential. Note that animal waste based biomass makes up only less than 5% while forest (41%) and waste (38%) sectors can contribute the greatest share of the potential (AEBIOM, 2011).

Similar to feedlot and dairy cattle, broiler chickens are raised in confinement buildings i.e. chicken houses on a bed of material that can be straw, sawdust, or rice hulls, upon which the

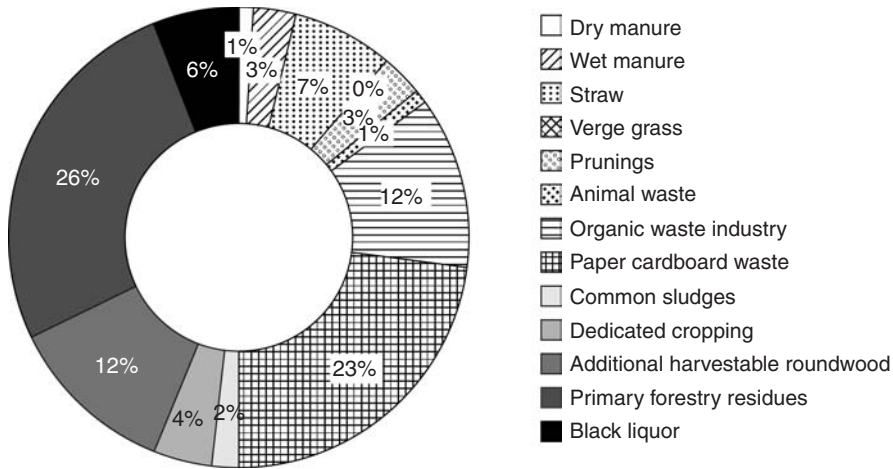


Figure 3.4. Summary of present EU biomass potential (Ktoe, kilo tonne oil equivalent) over categories (AEBIOM, 2011).

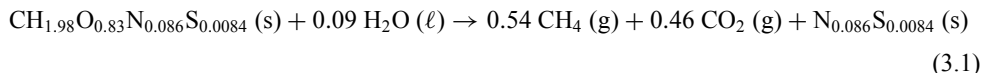
broiler chicken manure is deposited on the bedding, along with spilled feed and feathers over the life of the birds. Hence the waste material is termed poultry litter or broiler litter or litter biomass (LB). At the end of one or more growing cycles, the broiler litter is harvested by scraping out the chicken houses typically using a small wheel loader and must be stored, disposed of, or utilized.

Though the focus of the present chapter is on thermal energy (non-biological) conversion, a brief overview is presented on biological conversion, typically a slow process but producing medium quality gas (with *HHV* of almost 50% of natural gas).

3.3 BIOLOGICAL CONVERSION

3.3.1 Digestion

Anaerobic digestion is a biological process, which produces biogas. It is performed on the waste (at $T = 30\text{--}35^\circ\text{C}$ or at $T = 50\text{--}55^\circ\text{C}$) by two types of bacteria and it involves two steps: (i) breakdown of complex organics in the waste by acid-forming bacteria: into simpler compounds, including volatile acids (e.g. such as acetic and propionic); and (ii) the conversion of these acids by methane-producing bacteria into CO_2 and CH_4 called “biogas”. Typically both steps are performed in a single tank (GTI reports) and biogas contains mainly CH_4 ($\sim 60\%$), CO_2 ($\sim 35\%$) a mixture of H_2 , N_2 , NH_3 , CO and H_2S ($\sim 5\%$). The heat value of biogas is about 22350 kJ/m^3 for a mixture of $\text{CH}_4:\text{CO}_2:\text{inerts} = 60:35:5$. The investigations on digester-based energy conversion systems involving high moisture and/or high ash (HA) animal biomass (typically collected with soil, Fig. 3b) have mostly dealt with capturing biogas from biological systems such as anaerobic digesters. The percentage of CH_4 may be reasonably predicted using atom conservation equations for the reaction between digestible solids and H_2O (Annamalai and Puri, 2007):



Even though very little water is consumed (0.09 kmoles of H_2O per unique carbon atom in fuel (or empirical kmole of fuel), the bacteria can survive only in dilute slurry of water and digestible or volatile solids (VS). Element conservation yields 54% CH_4 and 46% CO_2 . One SI tonne of liquid manure with 5% dry matter (DM) produces about 20 m^3 biogas (Gregersen, 2009). There were only 40 operational systems in this country as of June 2004 (USEPA, 2004). Further discussions of biological energy conversion of manure-based biomass solids can be found in Meyer (2003), Matthews *et al.* (2003) and Schmidt *et al.* (2000). The digester efficiency is defined as the ratio of volatile solids (VS) converted into gas to VS fed in. For onion waste the digester efficiency is about 54% (Romano, *et al.*, 2004; Gunaseelan, 1997, 2004).

Up to 162 digestion systems were operating in the USA as of 2010 generating 450 million kWh (402 million as electricity and others as supplemental fuel, mixed with natural gas; 2.8 million barrels or equivalent to 25,000 homes per year i.e. average power consumption per home 20.5 kW) with 15 new digesters every year (Agstar Bulletin 2011; also see GTI reports). Digesters produce a renewable fuel in the form of CH_4 which also has a higher global warming potential when compared to CO_2 (20 times the global warming potential (GWP) compared to CO_2). Thus approximately 246,000 tonnes of CO_2 avoided; by capturing CH_4 and CO_2 in digester (as opposed to releasing CH_4 and CO_2 during atmospheric natural digestion), 1.1 million tonnes of CO_2 equivalent is destroyed. The majority of the plug flow reactors operate at mesophilic temperatures of about $35\text{--}40^\circ\text{C}$; others include covered lagoons; and about 25% of them co-digest with other organic wastes (food waste, agricultural wastes, cheese whey, etc.). Typical yields are as listed in Table 3.1.

3.3.2 Fermentation

The biomass can also be fermented to yield liquid alcohol fuels. If one assumes that 50% biomass is cellulose and all cellulose is converted into fermentable glucose, then with reaction $\text{C}_6\text{H}_{12}\text{O}_6 + 3\text{H}_2\text{O} [\text{L}] = 3\text{C}_2\text{H}_5\text{OH} [\text{L}] + 3\text{O}_2$ or $1\text{ kg cellulose} + 0.3\text{ kg of H}_2\text{O} = 0.77\text{ kg}$

Table 3.1. Biogas yields from different biomass.

Feedstock (manure)	CH ₄ [Yield, liters/ liter of VS added]
Dairy	0.034–0.118
Beef	0.055–0.082
Swine	0.058–0.111
Wheat stems	0.071
Wheat roots	0.047
Tomato	0.060

Table 3.2. Estimation of growth of biomass with 6% conversion efficiency.

Solar radiation and biomass growth	
1 gallon in m ³	0.003785
Feed density [kg/m ³]	800
Ethanol density [kg/liter (lb/gallon)]	0.788 (6.6)
HHV ethanol [MJ/kg (BTU/lb)]	167 (76000)
Solar irradiance [W/m ²]	1200
Conversion efficiency [%]	6
HHV biomass [kJ/kmole]	2801000
Molecular weight biomass	180
Cellulose% in biomass	50
Conversion to ethanol [kg/g glucose]	0.77
Cellulose to fermentable glucose	1
Biomass production [tonnes/hectare/year]	1459
Glucose [tonnes/hectare per year]	730
Ethanol production [tonnes/hectare]	562
Ethanol production [gallons/hectare]	185525
Ethanol [kg per tonne biomass]	385
Ethanol [gallon per tonne biomass]	127

ethanol + 0.53 kg O₂, ethanol production per tonne biomass is 125 gallons per tonne of biomass which is close to the reported theoretical value of 124 gallons/dry tonne of corn grain (Ragauskas). With 1 hectare = 10,000 m², and solar irradiation of 1200 W/m² and photosynthesis efficiency of 6%, the biomass production is 1460 tonnes per year per hectare assuming a heat value of 2,800,000 kJ/kmole, and with a molecular weight $M = 180$ kg/kmole. Comparing it with switch grass whose production is 37 tonnes per hectare per year, the maximum ethanol yield is 48.1 m³ (183,000 gallons) per hectare per year with a heating value (HV) of 7.37 kJ/m³ (28,000 kJ/gallon). With a higher heating value (HHV) of gasoline about 32.9 kJ/m³ (125,000 kJ/gallon), 1 liter of ethanol is equivalent to 0.22 liter of gasoline. Estimation of biomass growth with 6% conversion efficiency and the yield of ethanol from biomass are tabulated in Table 3.2.

3.4 THERMAL ENERGY CONVERSION

Although it may be a seemingly unrelated sector of American industry, researchers at Texas A&M have contended that energy production facilities, particularly coal-fired power plants, can benefit from co-firing of animal-wastes based biomass with coal. It can also minimize the CO₂

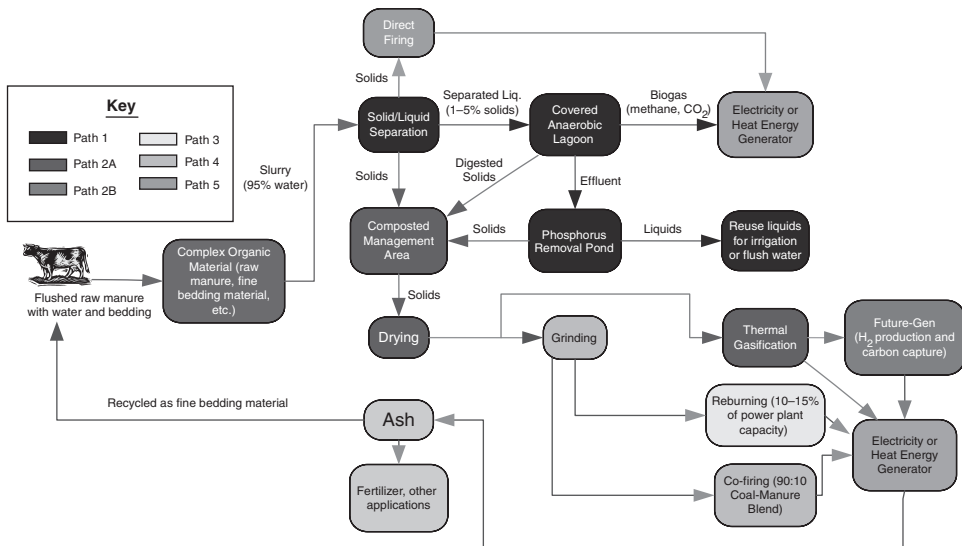


Figure 3.5. Five different paths for heat and electrical energy production from CB (adopted from Annamalai *et al.*, 2007a).

emissions by reducing the amount of fossil fuels used for heat and energy and the resulting emissions from fossil fuel power plants. Nitrogen oxides (NO_x), sulfur oxides (SO_x), mercury (Hg), and particulates have all been scrutinized emissions from coal-fired power plants, and restrictions on these products of combustion will probably continue to rise. Of course, animal biomass combustion will not solve global climate change alone; however, as discussed by (Pacala *et al.*, 2004), biomass combustion can be one of many wedges of advancement that can create an energy economy capable of sustaining our climate and our way of life. Direct combustion of biomass, combustion basics including stoichiometry, excess air, underfire and over fire air are dealt in Chapter 5 of this book (Desideri and Fantozzi, 2013).

There is also a great potential in the European Union (EU) to use animal waste based biomass to co-fire in existing coal-fired power plants. In 2011, the 27 EU member countries had a total cattle livestock of over 87 million with more than 23 million dairy cows. The animal numbers are projected to shrink because cattle herds are getting more productive. Annual reductions are estimated at 1.1% in 2012 to an 84.4 million head (TX PEER, 1998). The corresponding manure produced by cattle in 2009 was nearly 1300 million tonnes (Osei *et al.*, 2000). Five different paths for energy production from cattle biomass (CB) or any suitable animal wastes are illustrated in Figure 3.5 (Carlin *et al.*, 2007):

- Biological conversion
 1. Biogas and bio-liquid fuels
- Thermal conversion
 2. Direct slurry combustion (Carlin *et al.*, 2007)
 3. Co-firing of dried solids with coal
 4. Reburn
 5. Gasification.

The utilization of animal manure in combustion/gasification facilities can help ease the impacts large CAFOs, including dairies, have on the environment.

3.5 FUEL PROPERTIES

The overall purpose of this chapter is to summarize the fuel properties and current state of the art in developing environmentally benign thermal conversion or non-biological technologies (gasification, co-firing, and reburn, etc.) and they are presented in order to show how animal wastes can serve as a fossil fuel supplement, reduce GHG, dispose of the waste, and reduce NO_x emissions to convert low-value inventories of animal wastes into renewable energy.

The emissions (NO_x , SO_x), flame temperatures, and thermal energy outputs from burning biomass are required to determine the effectiveness and profitability of biomass energy conversion systems. However, in order to estimate these outputs, fuel properties of both coal, a widely used fossil fuel, and biomass must be known.

3.5.1 Proximate and ultimate analyses

The results of the proximate, ultimate (or elemental), and heat value analyses of the fossil and various animal waste based biomass fuels and coals are presented in Table 3.3. In general, the cattle biomass fuels are higher in ash, lower in heat content, higher in moisture, and higher in nitrogen and sulfur (which can cause air pollution) compared to the Texas and Wyoming coals. The *HV* of a fuel is the amount of heat released when a unit (mass or volume) of the fuel is burned. Typically, bomb calorimeters are used to determine the *HV*. Table 3.3 tabulates the higher or gross heat values of animal-waste-biomass (AWB) (Table 3.3). Generally, the *HHV* of CB on a dry, ash-free basis (DAF) tends to be between 18,000 and 22,000 kJ/kg (average about 20,000 kJ/kg) depending on the animal's feed ration (Sweeten *et al.*, 2003) while coals on DAF basis yield about 30,000 kJ/kg. Since DAF *HHV* is almost constant, it is the moisture and ash, which reduce the heat value and affect the flame temperatures as shown in Figure 3.5.

Using ultimate analyses, one can determine the empirical chemical formula. If the overall carbon content of gasoline is 82.6% (by mass) and hydrogen is 17.4%, then the empirical formula is given as $\text{C} = (82.6/12.01) = 6.88$, $\text{H} = 17.23$ or the empirical formula is $\text{C}_{6.88}\text{H}_{17.23}$ or after normalization with C atoms, $\text{CH}_{2.5}$. Since AnB and AgB contain C, H, O, N and S, the empirical formulae contain all these 5 atoms. Table 3.3 lists the empirical chemical formula for AgB and AnB fuels. The feedlot manure is collected from pens using wheel loaders, and is composted in windrows with composting unit. Manure is termed as raw if samples were collected from each windrow on day 1 (raw FB or unprocessed manure), partially composted, (or PC) if collected on day 31 and finished-composted, or FiC if collected on day 125. The composting helps in improving the homogeneity of the biomass.

Cattle biomass typically contains 1–3% nitrogen depending on the type of biomass, while coals generally contain up to 1% nitrogen, which is called fuel nitrogen depending on the rank of coal (Annamalai *et al.*, 2003a). The N content in fuels is of extreme importance since typically higher fuel N results in higher NO_x . Fuel nitrogen is released as a mixture of HCN, NH_3 and N_2 from coal and biomass. The NO_x generated from fuel N compounds is termed as fuel NO_x while the NO_x from atmospheric N_2 is referred to as thermal NO_x . For most coal-fired units, thermal NO_x contributes about 25% of the total NO_x emission, and fuel NO_x contributes the other 75% of the total (Annamalai *et al.*, 2003b). The AgB fuels contain a lower amount of N compared to coals. The reduction in NO_x when agricultural biomass (typically lower N content) is blended with coal occurs due to the following reasons: (i) lower N in AgB, (ii) reduced local O_2 due to higher VM, (iii) more N in the form of NH_3 than HCN since reduction via $\text{NH}_3 + \text{NO}_x$ is more rapid compared to $\text{HCN} + \text{NO}_x$ but it is noted that the lower N content in biomass will produce a lower amount of NH_3 . Thus Tillman *et al.* (2000) examined co-fired coal with low nitrogen AgB and showed that NO_x can be reduced by co-firing due to reduced N in blend; thus, NO_x was reduced simply by reducing the nitrogen loading to the furnace. However the reported amount of NO_x reduction (measured trend line) was greater than expected based on theoretical data (Fig. 3.6) since higher volatile matter in AgB (almost 80%) depletes the local O_2 rapidly resulting in lesser availability of O_2 for fuel N oxidation to NO. Thus Figure 3.6 shows that lower N in blend, the greater the NO_x

reduction in kg/GJ of heat released. However, since AnB contains more N compared to coal, there is a concern for increased NO_x emission during direct combustion. As seen later the N in AnB is mostly of urea type, which may help in better reduction of NO_x under appropriate temperature and oxygen %.

In Figure 3.7 it may be seen that raw FB, partially composted (PC) FB, fully/finished composted (FiC) FB, and cattle ration (cattle feed) all fall under this DAF *HHV* range. Similar results are also found when blending 5% crop residues with each FB fuel (Sweeten *et al.*, 2006).

3.5.2 Empirical formula for heat values

3.5.2.1 The higher heating value per unit mass of fuel

The gross or higher heating values *HHV* for coals can also be empirically obtained by using the Dulong equation (Annamalai and Puri, 2007), namely:

$$HHV [\text{kJ/kg}] = 33800 Y_C + 144153 Y_H - 18019 Y_O + 9412 Y_S \quad (3.2)$$

where Y_C, Y_H, Y_N, Y_O and Y_S are mass fractions of C, H, N, O and S.

Another relation due to Mott and Spooner is (Mason and Gandhi, 1980):

if $O < 15\%$

$$HHV [\text{kJ/dry kg}] = 103.5 C\% + 1418.3 \times H\% + 94.2 S\% - 145.1 \times O (\text{organic})\% \quad (3.3)$$

if $O > 15\%$

$$HHV [\text{kJ/dry kg}] = 103.5 \times C\% + 1418.3 \times H\% + 94.2 \times S\% - \{153.2 - 72 \times O\%/(100 - A\%)\} \times O\% \quad (3.4)$$

Here A = ash content.

Channiwalla (1992) considered over 200 species of biomass and fitted the following equation to the data:

$$HHV [\text{kJ/dry kg}] = 34910 Y_C + 117830 Y_C - 10340 Y_O - 21110 Y_A + 10050 Y_S - 1510 Y_N \quad (3.5)$$

The experimental data have an error of about 1.5%.

Boie empirical equation for *HHV* of any fuel $\text{C}_x\text{H}_y\text{N}_z\text{O}_w\text{S}_s$ (Annamalai and Puri, 2007):

$$HHV [\text{kJ/kmole}] = 422272 \times C + 117387 \times H - 155371 \times O + 100480 \times N + 335508 \times S \quad (3.6)$$

where C, H, O, N and S are the number of carbon, hydrogen, oxygen, nitrogen and sulfur atoms respectively in the fuel. The same equation can be used to determine the stoichiometric oxygen in kg per empirical kg of fuel:

$$\nu_{\text{O}_2} = 32 \{C + H/4 - (1/2)O + S\} = 32 C \{1 + (H/C)/4 - (1/2)(O/C) + (S/C)\} \quad (3.7)$$

$$HHV [\text{kJ/kg}] = C\{422272 + 117387 \times (H/C) - 155371 \times (O/C) + 100480(N/C) + 335508 \times (S/C)\} \quad (3.8)$$

Based on the Boie equation, the enthalpy of formation can be derived as:

$$\bar{h}_{F,f}^0 = 28752 \times \{C - 0.888 \times H - 6.168 \times O + 6.199 N + 1.337 S\} [\text{kJ/kmole}] \quad (3.9)$$

Table 3.3. Fuel Properties (adopted from Sweeten *et al.*, 2006 and TAMU, 2006).

Fuel	Type	Source	Ash	Dry loss	FC	VM	C
Coal	ar	T1: Fuel Properties	5.3300	15.1200	42.3800	37.1700	60.3000
Litter biomass	ar	T1: Fuel Properties	26.8100	11.6200	10.9100	50.6500	28.4400
Sewage sludges in Thailand (C1)	dry	Predicting the heating values of sewage sludges in Thailand	38.4000	6.1000	8.6000	53.0000	31.1000
Sewage sludges in Thailand (C2)	dry	Predicting the heating values of sewage sludges in Thailand	42.0000	5.1000	6.7000	51.2000	27.5000
Sewage sludges in Thailand (C3)	dry	Predicting the heating values of sewage sludges in Thailand	43.0000	5.4000	7.0000	50.0000	26.4000
Sewage sludges in Thailand (C4)	dry	Predicting the heating values of sewage sludges in Thailand	48.4000	6.4000	4.0000	47.6000	23.9000
Sewage sludges in Thailand (C5)	dry	Predicting the heating values of sewage sludges in Thailand	51.8000	3.7000	6.0000	42.2000	20.9000
Sewage sludges in Thailand (C6)	dry	Predicting the heating values of sewage sludges in Thailand	61.8000	4.1000	3.7000	34.5000	18.0000
Sewage sludges in Thailand (C7)	dry	Predicting the heating values of sewage sludges in Thailand	56.0000	3.4000	5.0000	39.0000	19.5000
Sewage sludges in Thailand (C8)	dry	Predicting the heating values of sewage sludges in Thailand	63.5000	3.9000	3.2000	33.3000	14.5000
Sewage sludges in Thailand (C9)	dry	Predicting the heating values of sewage sludges in Thailand	64.0000	3.7000	3.1000	32.9000	15.3000
Sewage sludges in Thailand (C10)	dry	Predicting the heating values of sewage sludges in Thailand	67.6000	3.2000	1.8000	30.6000	12.7000
Sewage sludges in Thailand (C11)	dry	Predicting the heating values of sewage sludges in Thailand	72.9000	4.4000	2.2000	24.8000	10.6000
Sewage sludges in Thailand (H1)	dry	Predicting the heating values of sewage sludges in Thailand	39.4000	6.6000	5.1000	55.5000	26.7000
Sewage sludges in Thailand (H2)	dry	Predicting the heating values of sewage sludges in Thailand	40.6000	5.6000	6.8000	52.6000	29.6000
Sewage sludges in Thailand (H3)	dry	Predicting the heating values of sewage sludges in Thailand	45.9000	4.6000	6.5000	47.7000	25.5000
Sewage sludges in Thailand (H4)	dry	Predicting the heating values of sewage sludges in Thailand	45.7000	6.9000	3.9000	50.4000	25.0000
Sewage sludges in Thailand (H5)	dry	Predicting the heating values of sewage sludges in Thailand	60.2000	4.6000	3.2000	36.6000	19.0000
Sewage sludges in Thailand (I1)	dry	Predicting the heating values of sewage sludges in Thailand	42.3000	5.2000	3.2000	54.5000	25.1000
Sewage sludges in Thailand (I2)	dry	Predicting the heating values of sewage sludges in Thailand	51.6000	5.0000	2.8000	45.6000	22.6000

ar: as received

H	N	O	S	HHV, kJ/kg	HHV-DAF Boie, kJ/kg	HHV-DAF, kJ/kg	Chemical formula
3.6200	0.9600	14.5000	0.2300	23710	30025	29805	CH _{0.7139} N _{0.0136} O _{0.1805} S _{0.0014}
3.7100	3.0350	22.7900	0.6600	12060	19564	19587	CH _{1.5512} N _{0.0915} O _{0.6015} S _{0.0087}
4.2000	3.3000	24.3000	1.1000	13900	21824	22565	CH _{1.6059} N _{0.0910} O _{0.5865} S _{0.0132}
4.1000	4.0000	23.3000	1.1000	13200	21099	22759	CH _{1.7729} N _{0.1247} O _{0.6360} S _{0.0150}
4.1000	4.3000	23.7000	0.9000	12600	20673	22105	CH _{1.8467} N _{0.1396} O _{0.6739} S _{0.0128}
3.9000	3.8000	21.8000	1.3000	11000	21111	21318	CH _{1.9404} N _{0.1363} O _{0.6847} S _{0.0204}
3.4000	3.3000	21.7000	0.9000	10100	19077	20954	CH _{1.9344} N _{0.1354} O _{0.7794} S _{0.0161}
2.9000	2.3000	16.7000	0.8000	9400	21140	24607	CH _{1.9158} N _{0.1095} O _{0.6964} S _{0.0166}
3.2000	3.1000	19.4000	0.8000	8700	19778	19773	CH _{1.9514} N _{0.1363} O _{0.7468} S _{0.0154}
2.6000	2.6000	18.1000	1.2000	6900	17539	18904	CH _{2.1322} N _{0.1537} O _{0.9370} S _{0.0310}
2.5000	2.3000	17.7000	0.5000	6500	18108	18056	CH _{1.9430} N _{0.1289} O _{0.8684} S _{0.0122}
2.0000	1.8000	17.5000	0.6000	5700	15509	17593	CH _{1.9430} N _{0.1289} O _{0.8684} S _{0.0122}
2.0000	1.6000	15.7000	0.4000	4300	16491	15867	CH _{2.2436} N _{0.1294} O _{1.1118} S _{0.0141}
4.0000	4.3000	27.5000	0.7000	13300	18697	21947	CH _{1.7814} N _{0.1381} O _{0.7731} S _{0.0098}
4.6000	5.0000	21.5000	1.0000	12800	23212	21549	CH _{1.8479} N _{0.1448} O _{0.5452} S _{0.0127}
3.9000	4.2000	21.7000	1.0000	12400	21145	22921	CH _{1.8186} N _{0.1412} O _{0.6388} S _{0.0147}
3.8000	3.7000	24.3000	0.8000	11100	19941	20442	CH _{1.8074} N _{0.1269} O _{0.7296} S _{0.0120}
3.0000	2.7000	16.8000	1.2000	8200	21606	20603	CH _{1.8775} N _{0.1218} O _{0.6637} S _{0.0237}
4.0000	3.8000	26.1000	0.9000	10900	18912	18891	CH _{1.8950} N _{0.1298} O _{0.7805} S _{0.0134}
3.2000	2.9000	20.3000	2.0000	9900	20259	20455	CH _{1.6837} N _{0.1100} O _{0.6742} S _{0.0332}

(Continued)

Table 3.3. Continued.

Fuel	Type	Source	Ash	Dry loss	FC	VM	C
Sewage sludges in Thailand (I3)	dry	Predicting the heating values of sewage sludges in Thailand	58.8000	4.7000	3.0000	38.2000	18.3000
Misc. manure	ar	n/a	36.3825	50.5000	2.3760	10.7910	9.7020
Sheep manure	ar	n/a	10.9098	47.8000	7.3080	34.0344	21.1932
Mortality Biomass source: Brent Auvermann (before treatment)	ar	Properties of the fuels (MB)	34.2000	0.9600	10.4700	54.3700	38.4500
Cofired coal	dry	T3: Proximate, ultimate and ash analyses of coal, pine shavings, and animal waste	14.7000	5.0000	61.1400	24.1600	72.7500
Pine shavings	dry	T3: Proximate, ultimate and ash analyses of coal, pine shavings, and animal waste	0.1000	45.0000	15.2000	84.7000	49.1000
Reed Canary Grass	dry	T3: Proximate, ultimate and ash analyses of coal, pine shavings, and animal waste	4.1000	65.2000	19.8000	76.1000	45.8000
Sheep manure	dry	T3: Proximate, ultimate and ash analyses of coal, pine shavings, and animal waste	20.9000	47.8000	14.0000	65.2000	40.6000
Dairy free-stall	dry	T3: Proximate, ultimate and ash analyses of coal, pine shavings, and animal waste	62.3000	70.3000	7.1000	30.6000	22.1000
Misc. manure	dry	T3: Proximate, ultimate and ash analyses of coal, pine shavings, and animal waste	73.5000	50.5000	4.8000	21.8000	19.6000
DB soil surface	ar	n/a	59.9100	12.2100	3.9200	23.9900	18.0200
DB seperated solids	ar	n/a	14.9300	25.2600	13.0000	46.8800	35.2000
Texas lignite	ar	n/a	11.5000	38.3000	25.4000	24.8000	37.2000
Wyoming sub-bituminous	ar	n/a	5.6000	32.9000	33.0000	28.5000	46.5000

Thus an approximate method based on the Boie heat value exists to compute h_f of any empirical fuel. If only mass fractions of C, H, N, O and S are known as Y_C , Y_H , Y_N , Y_O and Y_S , then the higher heating value of the fuel becomes:

$$HHV_F [\text{kJ/kg}_{\text{fuel}}] = 35160 Y_C + 116225 Y_H - 11090 Y_O + 6280 Y_N + 10465 Y_S \quad (3.10)$$

One can deduce the lower or net heat value (LHV) when hydrogen in water is excluded giving:

$$LHV_F [\text{kJ/kg}_{\text{fuel}}] = 35160 Y_C + 94438 Y_H - 11090 Y_O + 6280 Y_N + 10465 Y_S \quad (3.11)$$

H	N	O	S	HHV, kJ/kg	HHV-DAF Boie, kJ/kg	HHV-DAF, kJ/kg	Chemical formula
3.4000	1.8000	18.7000	1.8000	9000	20907	21845	CH _{2.2093} N _{0.0843} O _{0.7670} S _{0.0368}
1.2375	0.4950	1.6335	0.0495	3585	35730	27330	CH _{1.5167} N _{0.0437} O _{0.1264} S _{0.0019}
2.6622	1.0962	16.0254	0.3132	8372	21455	20275	CH _{1.4937} N _{0.0443} O _{0.5676} S _{0.0055}
3.9700	0.2900	22.7100	0.0500	12774	24118	19701	CH _{1.2278} N _{0.0065} O _{0.4433} S _{0.0005}
3.9100	1.5000	4.8700	2.2700	30512	35070	35770	CH _{0.6391} N _{0.0177} O _{0.0502} S _{0.0117}
6.4000	0.2000	44.0000	0.2000	19475	19876	19494	CH _{1.5500} N _{0.0035} O _{0.6727} S _{0.0015}
45.8000	1.0000	42.9000	0.1000	16838	19300	17558	CH _{1.5837} N _{0.0187} O _{0.7031} S _{0.0008}
5.1000	2.1000	30.7000	0.6000	16037	21455	20274	CH _{1.4937} N _{0.0443} O _{0.5676} S _{0.0055}
2.9000	1.1000	11.5000	0.1000	8836	26380	23438	CH _{1.5604} N _{0.0427} O _{0.3906} S _{0.0017}
2.5000	1.0000	3.3000	0.1000	7243	35730	27332	CH _{1.5167} N _{0.0437} O _{0.1264} S _{0.0019}
1.4500	1.1500	7.0700	0.1900	4303	26260	15434	CH _{0.9568} N _{0.0547} O _{0.2945} S _{0.0039}
3.1200	1.9300	19.1500	0.4300	12817	23455	21430	CH _{1.0540} N _{0.0470} O _{0.4084} S _{0.0046}
2.1000	0.7000	9.6000	0.6000	14290	29009	28466	CH _{0.6713} N _{0.0161} O _{0.1937} S _{0.0060}
2.7000	0.7000	11.3000	0.3000	18194	29772	29584	CH _{0.6905} N _{0.0129} O _{0.1824} S _{0.0024}

Correlation for adiabatic flame temperature with ash and moisture content is shown and plotted in Figure 3.8.

Figure 3.9 shows the higher heat or gross heat value of C-H-O fuel in kJ per kg of fuel.

3.5.2.2 The higher heat value per unit stoichiometric oxygen

The heat value per unit stoichiometric oxygen (ν_{O_2}) defined as:

$$HHV_{O_2} = \frac{HHV}{\nu_{O_2}} \quad (3.12)$$

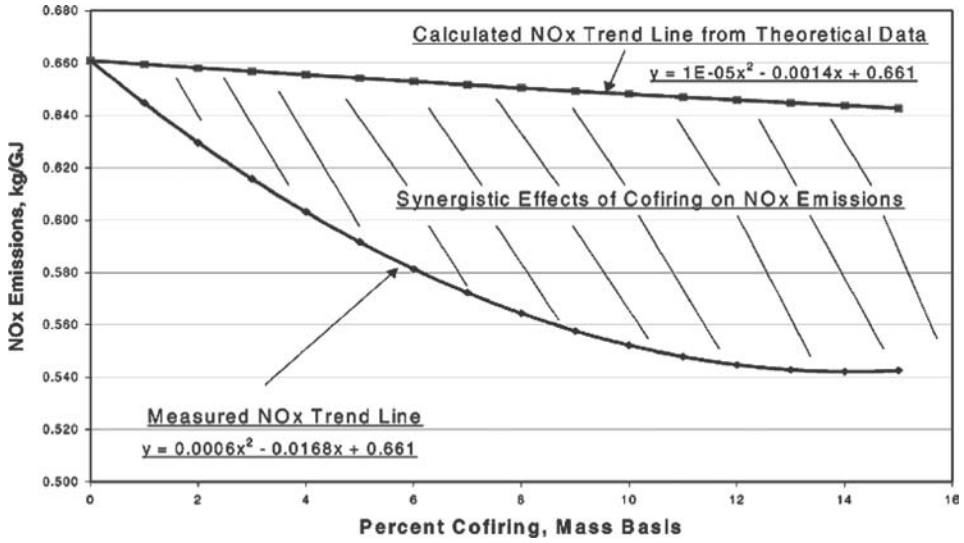


Figure 3.6. Synergistic NO_x reduction from co-firing biomass (adopted from Tillman, 2000).

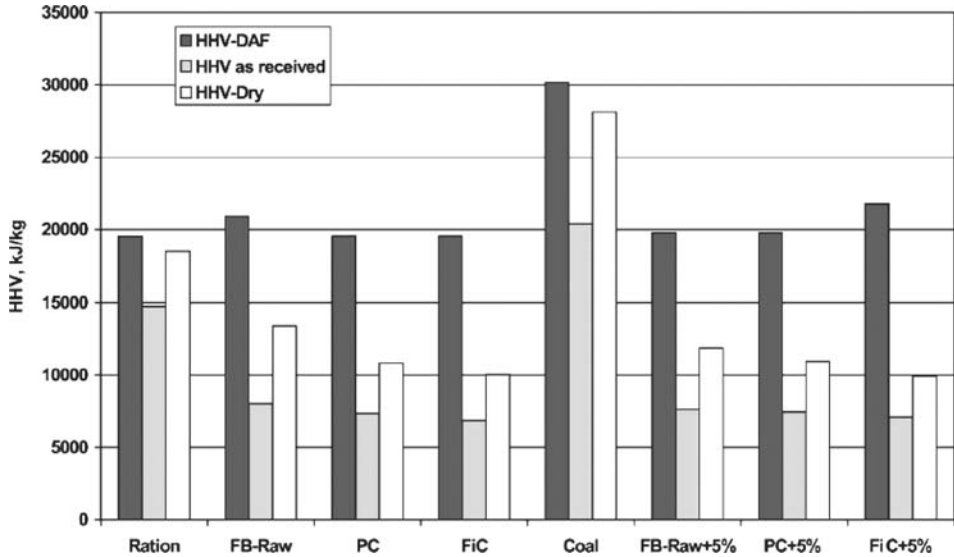


Figure 3.7. Higher heating values HHV for cattle ration, raw FB, partially composted FB, finished composted FB, coal, and respective FB + 5% crop residue blends (adopted from Sweeten et al., 2003).

It is well known that the HHV_{O_2} is almost constant for most fuels. For Boie equation, the HHV_{O_2} is given as:

$$\text{HHV}_{\text{O}_2} [\text{kJ/kg of O}_2] = \{422272 + 117387 \times (\text{H/C}) - 155371 \times (\text{O/C}) + 100480(\text{N/C}) + 335508 \times (\text{S/C})\} / (32\{1 + (\text{H/C})/4 - (1/2)(\text{O/C}) + (\text{S/C})\}) \quad (3.13)$$

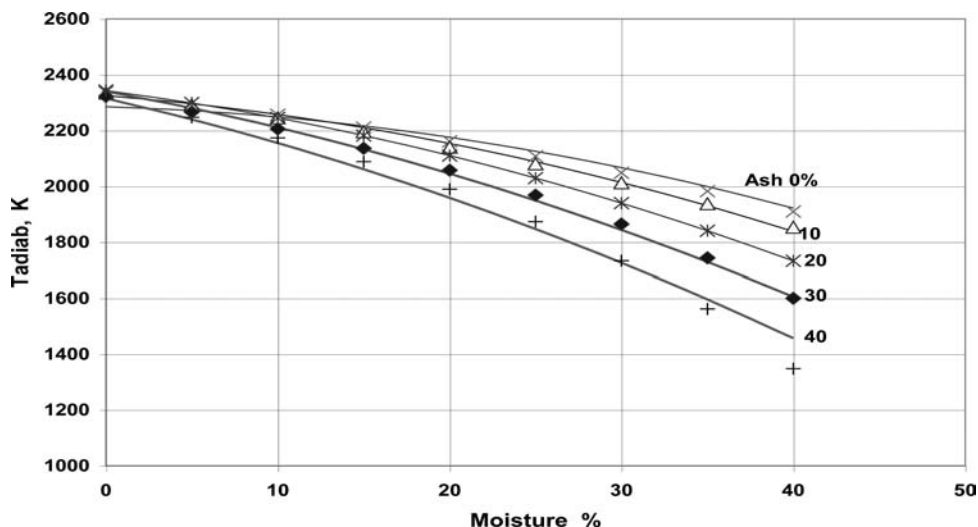


Figure 3.8. Correlation of adiabatic flame temperature with moisture and ash contents; $T_{\text{adiabatic}} [\text{K}] = 2285 - 1.8864 \times \text{H}_2\text{O} + 5.0571 \times \text{Ash} - 0.3089 \times \text{H}_2\text{O} \times \text{Ash} - 0.1802 \times \text{H}_2\text{O}^2 - 0.1076 \times \text{Ash}^2$, H_2O and Ash in fractions; multiply $T_{\text{adiabatic}}$ in K by 1.8 to obtain T (Annamalai *et al.*, 2007b; Sami *et al.*, 2001).

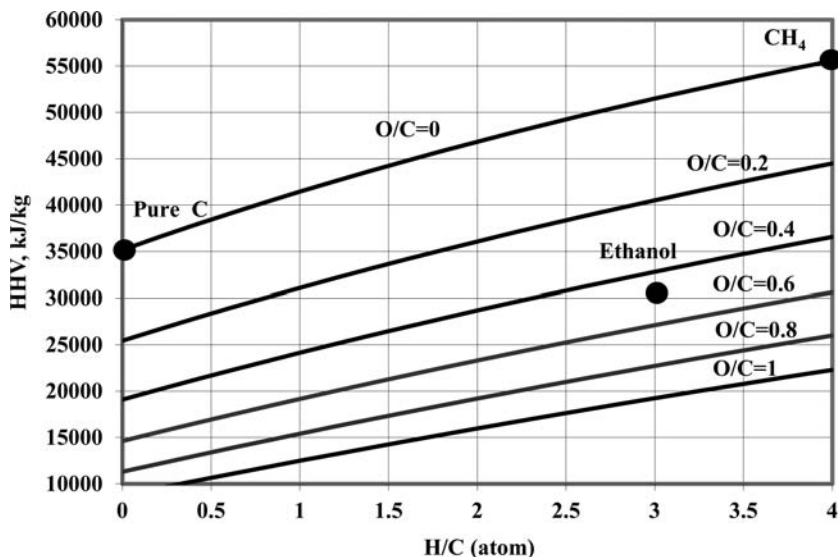


Figure 3.9. Variation of HHV with H/C and O/C in C-H-O fuels.

Ignoring S and N, trace elements in fuel, Figure 3.10 plots HHV_{O_2} , in kJ per kg of oxygen as HHV/ν_{O_2} constant. It is apparent that the HHV per unit mass of O_2 burned is approximately the same of about 14250 kJ/kg of oxygen (18.6 kJ/SATP liter of oxygen, where SATP means at standard atmospheric temperature and pressure) or 3280 kJ/kg stoich air (3.9 kJ/SATP liter of air) for most fuels. For methane, the literature states that HV per unit O_2 is 13550 kJ per kg of O_2 (17.7 kJ/SATP liter of O_2) while Boie based equation yields 13934 kJ/kg of O_2 . For n-octane,

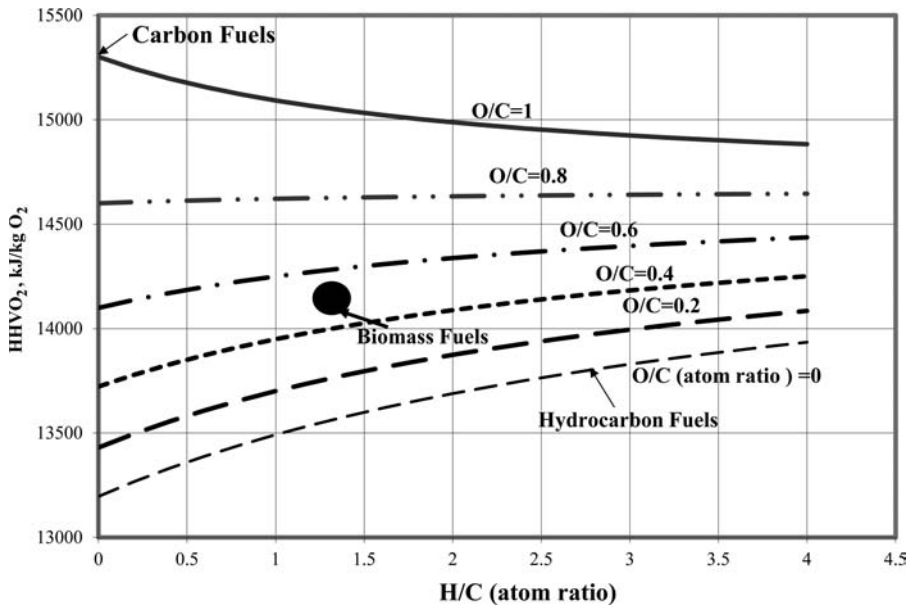


Figure 3.10. Variation of HHV_{O_2} in kJ/kg of O_2 with H/C and O/C in C-H-O fuels.

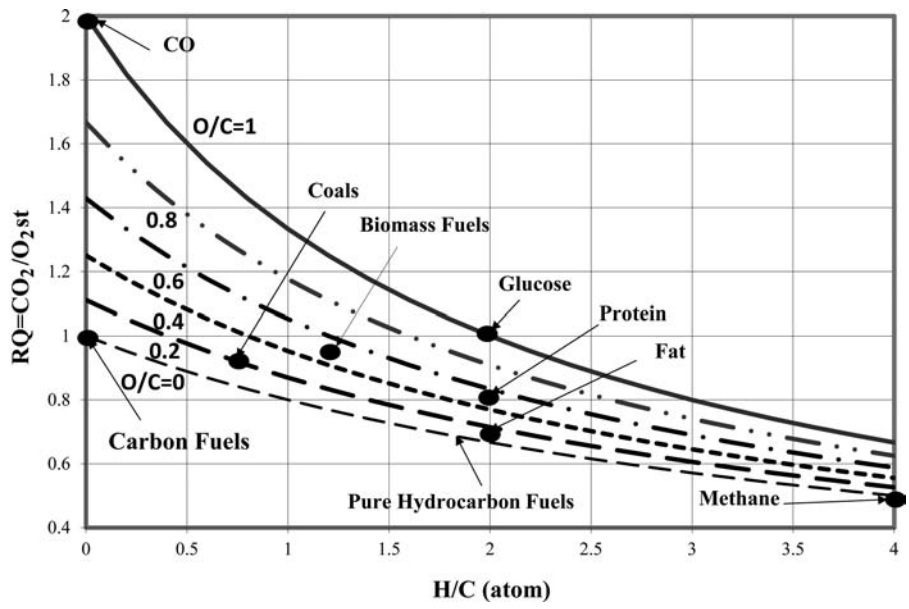


Figure 3.11. Variation of CO_2/O_{2st} with H/C and O/C in C-H-O fuels.

the value is 13640 kJ per kg of O₂ or 17.82 kJ/liter of O₂ (SATP) for CH₄ while Boie yields 13730 kJ/kg O₂ for Octane.

Figure 3.11 plots the respiratory quotient (RQ), a term used in biological literature (Annamalai and Silva, 2011) and defined as CO₂ per kmole of stoichiometric oxygen, an indication of global

warming potential) for various biomass fuels. Typically RQ is about 1 (which is same as that of glucose, $C_6H_{12}O_6$) for biomass fuels.

3.5.2.3 Heat value of volatile matter

In Figure 3.11 we see how H/C relates in fat, protein, biomass and coal. If the heat of pyrolysis is neglected, the heat of combustion of the coal can be represented as a combination of the contribution from the volatile matter (HV_{VM}) and the contribution from the fixed carbon (HV_{FC}) in relation to their mass percentages:

$$HV_{Coal} = HV_{VM} + HV_{FC} \quad (3.14)$$

If $FC = 1 - VM$ as in the case of dry ash-free (DAF) coals, one can correlate the heating values of volatiles HV_v to VM (Annamalai and Puri, 2007). The Volatile Matter Higher heating value (HHV_{VM}) was calculated using:

$$HHV_{VM} \cong \frac{(HHV - FC\% \cdot HHV_{FC})}{VM\%} \quad (3.15)$$

where HHV is the as received heating value, $FC\%$ is the amount of fixed carbon present in the fuel, HHV_{FC} is the higher heating value of the fixed carbon (enthalpy of formation/molecular weight), and $VM\%$ is the amount of volatile matter present in the fuel.

3.5.2.4 Volatile matter and stoichiometry

Assuming that coal is represented by $CH_{0.8}O_{0.1}$ and DB by $CH_{1.1}O_{0.4}$, Figure 3.12 and Figure 3.13 plot the fraction of C atom remaining as volatile matter in coal and DB and the stoichiometric oxygen per kg volatile matter for coal and DB; if coal releases less VM for given H/C and O/C, then less C atoms leave with VM and more remain in char; typically coal has 40–50% as VM and as such, the stoichiometric O_2 is about 2.5 kg per kg VM released; the DB has 80% VM and as such the stoichiometric O_2 is only about 1.5 kg/kg of VM and lower compared to coal volatiles due to high O/C ratio in DB. At the same time, the % O_2 consumed by coal during combustion of VM is only 50% while DB with VM consumes 78% of oxygen by the time all the volatile matter is burnt indicating that there is rapid depletion of O_2 when DB is blended with coal resulting in lower O_2 in the furnace which may lead to lesser NO_x . In general AgB and AnB fuels with high VM may result in lesser NO_x compared to coals.

3.5.2.5 Stoichiometric A:F

The mass based stoichiometric A:F ratio is simply the ratio of the minimum amount air required by fuel for complete combustion on a mass basis. This is calculated based on the empirical chemical formula derived from the ultimate analysis neglecting the moisture and ash in the fuel.

3.5.2.6 Flue gas volume

One can determine the volume of flue gas in m^3/GJ from the knowledge of ultimate analysis, Boie equation and reaction equations of biomass with O_2 supplied from air (Chapter 4, Annamalai and Puri, 2007). If the SATP is at $25^\circ C$, and 1 bar, then for any arbitrary $0 < O_2\% < 9\%$ (volume), a fit is given as:

$$\begin{aligned} \text{Flue gas STP volume, } m^3/GJ = & \{3.55 + 0.131 O_2\% + 0.018 \times (O_2\%)^2\}(H/C)^2 \\ & - \{27.664 + 1.019 O_2\% + 0.140 \times (O_2\%)^2\}(H/C) \\ & + \{279.12 + 10.285 O_2\% + 1.416 \times (O_2\%)^2\} \end{aligned} \quad (3.16)$$

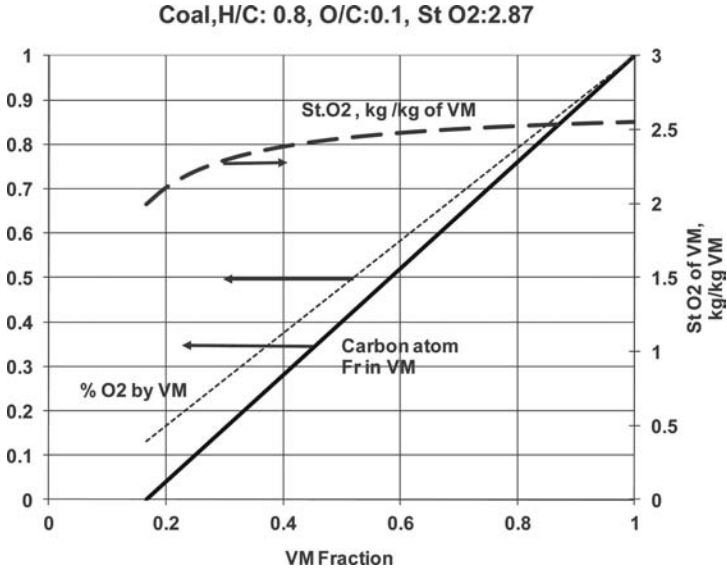


Figure 3.12. Fraction of C atoms remaining with VM fraction, coal.

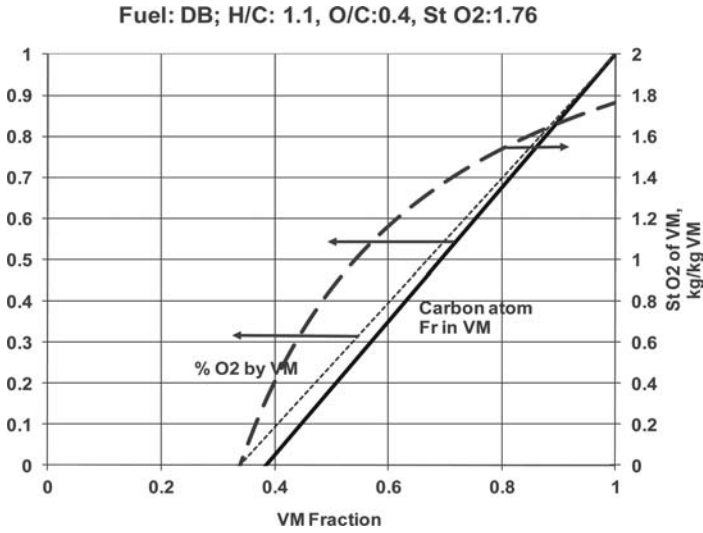


Figure 3.13. Fraction of C atoms remaining with VM fraction, Dairy Biomass (DB).

3.5.3 Fuel change and effect on CO₂

The CO₂ emission in kg/GJ of heat released is of extreme importance in ascertaining GWP of fuel particularly when fuels are switched. Based on the Boie equation, Figure 3.14 plots the CO₂ in g/MJ (or kg/GJ) for C-H-O fuels. It is clear that biomass has similar CO₂ emissions compared to coals even though it has less C% compared to coals but the heat value of biomass is correspondingly lower!

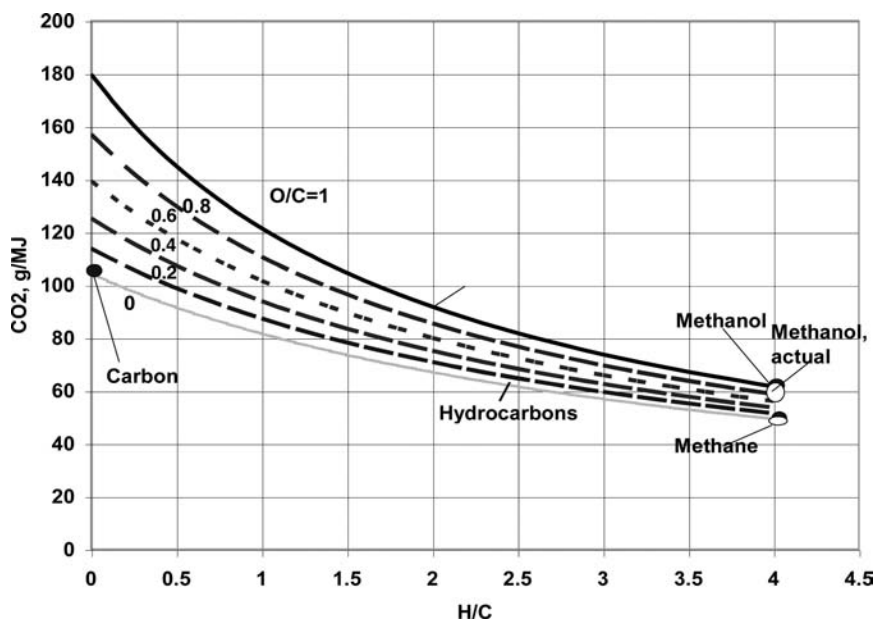


Figure 3.14. CO_2 emission in g/MJ (or kg/GJ) for C-H-O fuels. Multiply ordinate by 2.326 to get lb per mm BTU.

3.5.4 Air flow rate and multi-fuels firing

Similar $\text{O}_2\%$ in exhaust implies excess air% remain similar for most solid fuels (Lawrence, 2007). Since thermal output = $\text{HHV}_{\text{O}_2} \times \text{stoichiometric } \text{O}_2 \text{ flow rate} = \text{HHV}_{\text{air}} \times \text{stoichiometric air flow rate} = \text{HHV}_{\text{air}} \times \text{actual air flow rate} / (1 + x/100)$ where x is % excess air; thus when actual air flow rate is maintained the same, then one may switch the fuel and adjust the fuel flow rate such that same $\text{O}_2\%$ is maintained which ensures similar thermal output. In automobiles, when alternate fuels are used for combustion, same thermal energy input is assured when air flow is maintained the same and fuel flow is adjusted such that same $\text{O}_2\%$ is maintained in exhaust.

3.5.5 CO_2 and fuel substitution

Since HHV_{O_2} is constant for most fuels, then for given thermal input, the O_2 moles consumed remain the same; a fuel with higher RQ produces more CO_2 for the same thermal heat input! The reader is referred to Chapter 2 in this book on the basics of thermal energy conversion, stoichiometry, air fuel ratio and flame temperatures.

3.6 TGA STUDIES ON PYROLYSIS AND IGNITION

While the ultimate and proximate analyses provide information on the basic elements of fuel and quality of fuels (heat value, volatile matter, emission potential (based on N and S contents)), the temperature of the start and end pyrolysis, and rate of release of VM are provided by Thermo gravimetric Analyses (TGA). In addition, the modeling of pyrolysis, gasification, various energy conversion processes (see Chapter 2 of this book by Agarwal), co-firing, and reburn behavior and also understand the ignition behavior and NO_x reduction characteristics of biomass and coal fuel, fundamental pyrolysis and ignition experiments must be conducted to generate data on fuel properties. Experiments were conducted in a Thermo Gravimetric Analyzer/Differential Thermal Analyzer (TGA/DTA) in both N_2 and air environment.

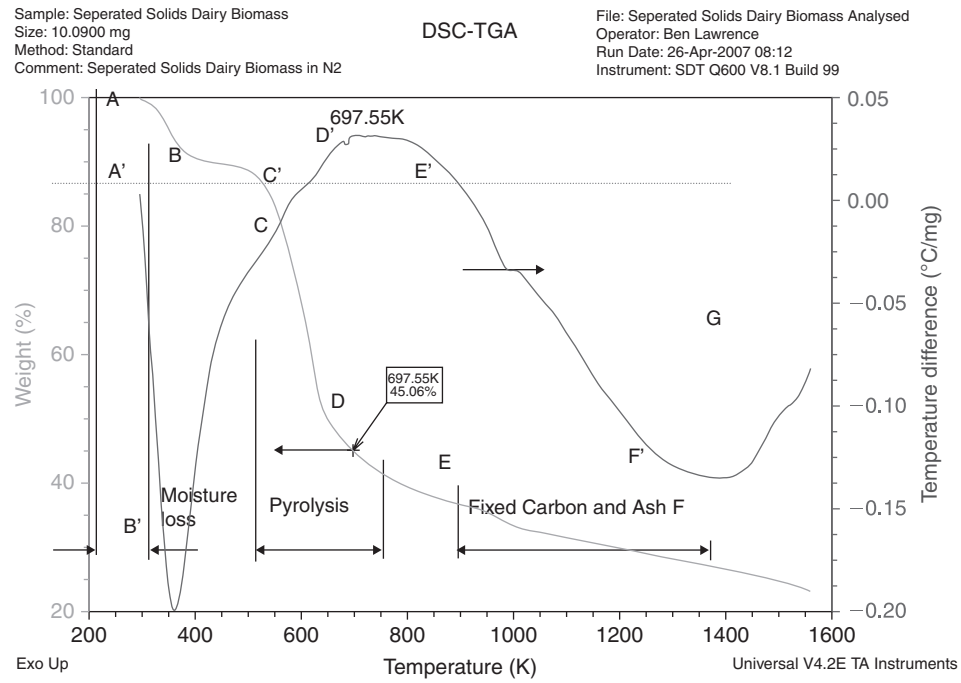


Figure 3.15. TGA and DTA trace of low ash (LA, typically collected from paved feedlots) partially composted (PC) LA-PC-DB-SepS. Note the data labels showing the peak of the DTA curve and the corresponding mass percent at that temperature (adopted from Lawrence, 2007).

3.6.1 Pyrolysis

Thermo gravimetric analyses on the coal and other biomass were performed using a TA SDT Q600 TGA-DSC instrument. Around 10 mg fuel sample was heated at a rate of 20 K/min from ambient to high temperature (above 1000°C) in an inert (nitrogen) environment. The mass of the sample as a function of temperature was recorded. All fuels were analyzed as received. A reference pan was also heated in the same furnace at the same rate. The temperature of the reference pan was recorded with the temperature of the sample pan. The difference in the temperatures between the two pans can be used to create a DTA trace (Martinez, 2012 and Lawrence, 2007)). Figure 3.15 gives the TGA (ABCDEWF) and DTA traces (A'B'C'D'E'F') for the fuels considered.

Point A marks the beginning of the traces. Point B (B' on DTA) marks the peak of the drying (endothermic) process. Point C marks the beginning of the pyrolytic exothermic. Point D marks the peak of the pyrolytic exothermic. Point E marks the end of the pyrolytic exothermic. Following pyrolysis, only fixed carbon and ash remained in the pan. Point F marks the end of the trace. Of particular interest are the temperatures at which pyrolysis began, ended, and the percentage of mass lost due to pyrolysis. The portion between points A and B on the TGA trace defines the amount of mass lost due to drying (moisture loss). The portion between points C and E on the TGA trace defines the amount of mass lost due to pyrolysis. The temperature and remaining mass at this point have been marked in Figure 3.15. The pyrolysis data for several fuels are summarized in Table 3.4.

3.7 MODEL

In this section, three different methods: Single Reaction Model, Conventional Arrhenius Method and parallel reaction model were employed to estimate the chemical kinetic parameters

Table 3.4. TGA analysis of several fuels (adopted from Lawrence, 2007).

Fuel	TXL	WYO	HA-PC-DB-SoilS	LA-PCDB-SepS
Moisture loss onset temperature [K]	373.09	375.71	367.45	386.19
Moisture mass [%]	24.12	20.92	4.678	8.89
Pyrolysis loss onset temperature [K]	637.93	657.15	529.23	513.6
Pyrolysis mass [%]	18.95	21.01	32.53	56.01
10% of pyrolysis mass [%]	1.895	2.101	3.253	5.601
Mass at 10% of pyrolysis mass [%]	73.985	76.979	92.069	85.509
10% pyrolysis mass loss temperature [K]	661.11	685.44	552.99	536.27
90% of pyrolysis mass [%]	17.055	18.909	29.277	50.409
Mass at 90% of pyrolysis mass [%]	58.825	60.171	66.045	40.701
90% Pyrolysis mass loss temperature [K]	748.78	759.83	1021.28	766.89
Peak pyrolysis mass [%]	61.9	66.21	45.06	81.74
Peak pyrolysis temperature [K]	698.68	702.5	697.55	749.21
FC and ash mass [%]	56.93	58.07	62.792	35.1
FC and ash loss onset [K]	774.07	786.56	1037.1	990.95
Ignition temperature [K]	544.42	571.78	509.43	526.06

of Biomass (Chen *et al.*, 2012b) so that the rate of pyrolysis and time scale for pyrolysis can be determined.

3.7.1 Single reaction model: conventional Arrhenius method

The single reaction model is given in the equation:

$$-\frac{dm_v}{dt} = k(T) \cdot m_v \quad (3.17)$$

where m_v is the mass of volatiles remaining in the sample and $k(T)$ is given by the Arrhenius expression (Annamalai and Puri, 2007):

$$k(T) = B \cdot \exp\left(\frac{-E}{RT}\right) \quad (3.18)$$

Separating variables and integrating equation (3.17) yields the following result:

$$-\ln\left(\frac{m_v}{m_{v0}}\right) = \int_0^t B \cdot \exp\left(\frac{E}{R \cdot T}\right) dt \quad (3.19)$$

where m_v is the mass of the volatiles at time t , $m_{v,0}$ is the initial mass of volatiles at $t = 0$, B is the pre-exponential factor, E is the activation energy, R is the universal gas constant, and T is the absolute temperature.

Since the temperature change with time is constant in TGA tests, the integral on the right side of equation can be rewritten as:

$$-\ln\left(\frac{m_v}{m_{v0}}\right) = \left(\frac{B}{\beta}\right) \cdot \left(\frac{E}{R}\right) \cdot \left\{ \frac{E_2(X)}{X} - \frac{E_2(X_0)}{X_0} \right\} \quad (3.20)$$

where $X = (E/RT)$, β is the rate of change for temperature with time (20 K/min), E_2 , second exponential integral (Abaramovitz and Stegun, 1970) given as:

$$E_2(X) = \{\exp(-X) - X \cdot E_1(X)\}, \quad (3.21)$$

$$E_1(X) \approx \frac{1}{X \cdot \exp(X)} \cdot \left(\frac{X^2 + a_1 \cdot X + a_2}{X^2 + b_1 \cdot X + b_2} \right)$$

where: $a_1 = 2.334733$, $a_2 = 0.250621$
 $b_1 = 3.330657$, $b_2 = 1.681534$

Using the expression for $E_1(X)$, the $E_2(X)$ can also be expressed as:

$$E_2(X) \approx \exp(-X) \left\{ \frac{(b_1 - a_1) \cdot X + (b_2 - a_2)}{X^2 + b_1 \cdot X + b_2} \right\} \quad (3.22)$$

Equation (3.20) presents the exact relation between m_v , volatiles remaining at temperature T and heating rate for SRM. The conventional Arrhenius plot of $\ln(m_v/m_{v0})$ vs. $1/T$ for extraction of E and B for the whole domain of pyrolysis is based on further approximations of equation (3.20). If $T \gg T_0$ (pyrolysis start temperature), then, $X \ll X_0$, and $E_2(X)/X \gg \gg E_2(X_0)/X_0$ and with equation (3.22), equation (3.20) becomes (Chen, 2012b):

$$-\ln\left(\frac{m_v}{m_{v0}}\right) \approx \left\{ \frac{B(E/R)}{\beta} \right\} \left[\frac{E_2(X)}{X} \right] \approx \left\{ \frac{BC(X)(E/R)}{\beta} \right\} \exp(-X) \quad (3.23)$$

$$C(X) = \left\{ \frac{(b_1 - a_1)X + b_2 - a_2}{X(X^2 + b_1X + b_2)} \right\}$$

Here $C(X)$ was introduced as a support vector. Taking the logarithm of equation (3.23):

$$\ln\left\{-\ln\left(\frac{m_v}{m_{v0}}\right)\right\} \approx \ln\left\{\frac{(E/R)B\{C(X)\}}{\beta}\right\} - \frac{E}{RT} \quad (3.24)$$

equation (3.24) becomes:

$$\ln\{-\ln(f)\} \approx A - \frac{E}{RT}, \quad (3.25)$$

where

$$f = \frac{m_v}{m_{v0}}$$

and $C(X)$ is roughly constant. As a result, the activation energy E and pre-exponential factor B can be determined from the slope and intercept of the linear plot $\ln(-\ln(m_v/m_{v0}))$. Figure 3.16 shows the Arrhenius plot for low ash partially composted separated solids dairy biomass.

3.7.2 Parallel Reaction Model (PRM)

The biomass consists of several components including hemicellulose, cellulose and lignin. Since the activation energy is related to the bond energy and bond energy varies widely within biomass fuels having multiple components, it can be assumed that the pyrolysis process consists of an infinite number of reactions proceeding in parallel with E ranging from 0 to infinity (Anthony *et al.*, 1973). The parallel reaction model (PRM), can also be called the distributed activation energy model with a large number of reactions in order to avoid confusion with the two or three single reactions proceeding in parallel. If $\delta m_{v,E}$ is the mass change within a short period of time dt having activation energy between E and $E + dE$, the rate of liberation of volatiles for a first order pyrolysis can be written as:

$$-\frac{d\{\delta m_{v,E}\}}{dt} = k_E \cdot (\delta m_{v,E}) \quad (3.26)$$

where the specific reaction constant k_E [1/s] is given by the Arrhenius expression:

$$k_E = B \cdot \exp\left(-\frac{E}{R \cdot T}\right)$$

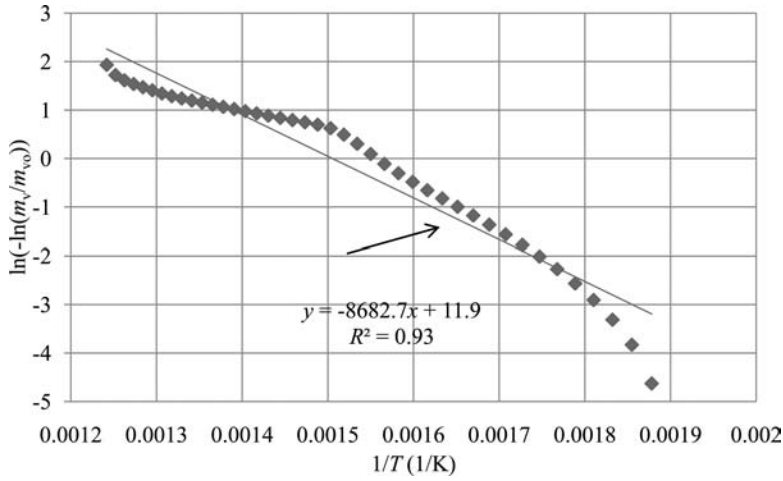


Figure 3.16. Arrhenius plot for LA-PC-DB-SepS.

where B and E are the pre-exponential factor and activation energy, respectively.

Assuming a Gaussian distribution, the fraction of initial total volatiles mass having activation energy between E and $E + dE$ can be expressed as:

$$\frac{\delta m_{v,E,0}}{m_{v,0}} = f(E)dE \quad (3.27)$$

where:

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(E - E_m)^2}{2 \cdot \sigma^2}\right) \quad (3.28)$$

and:

$$\int_0^{\infty} f(E)dE = 1 \quad (3.29)$$

where E_m is the mean activation energy, and σ is the standard deviation of activation energy. The Gaussian distribution indicates that 1% mass has activation energy within $E < E_m - 2.3\sigma$; these E values refer to low activation energy components of the volatiles. Similarly, 1% of mass corresponds to high activation energy components with $E > E_m + 2.3\sigma$. Thus 98% of mass is covered for $E_m - 2.3\sigma < E < E_m + 2.3\sigma$ while about 99.9% of the mass is located for E such that $E_m - 3\sigma < E < E_m + 3\sigma$. Assuming pre-exponential factor B is the same for all volatiles having activation energy $0 < E < \infty$ and equal to B and integrating over all possible positive values of E will provide the volatile fraction:

$$\left(\frac{m_v}{m_{v0}}\right) = \int_0^{\infty} \exp\left\{-\int_{T_0}^T \frac{B}{\beta} \exp\left(-\frac{E}{RT}\right) dT\right\} f(E)dE \quad (3.30)$$

With further rearranging, equation (3.30) becomes:

$$\frac{m_v(T)}{m_{v,0}} = \frac{1}{\sigma \cdot \sqrt{2\pi}} \cdot \int_{E_m-3\sigma}^{E_m+3\sigma} \exp\left\{-\frac{B}{\beta} \cdot \left[T \cdot E_2\left(\frac{E}{R \cdot T}\right) - T_0 \cdot E_2\left(\frac{E}{R \cdot T_0}\right)\right] - \frac{(E - E_m)^2}{2 \cdot \sigma^2}\right\} dE \quad (3.31)$$

Note: the limits of integration have been changed from 0, ∞ to $E_m \pm 3\sigma$ that covers 99.9% of total mass. Defining:

$$G(E, T) = \exp \left\{ -\frac{B}{\beta} \cdot \left\{ T \cdot E_2 \left(\frac{E}{R \cdot T} \right) - T_0 \cdot E_2 \left(\frac{E}{R \cdot T_0} \right) \right\} - \frac{(E - E_m)^2}{2 \cdot \sigma^2} \right\} \quad (3.32)$$

G can be represented as a 2D matrix for values of E between $E_m - 3\sigma$ and $E_m + 3\sigma$ and values of T between T_0 and T_n , where T_0 corresponds to temperature at the beginning of pyrolysis (99% VM remaining) and T_n corresponds to temperature at the end of pyrolysis (1% VM remaining), respectively (Martin, 2006; Chen, 2012b). With equation (3.32) in equation (3.31):

$$\frac{m_v(T)}{m_{v,0}} = \frac{1}{\sigma \cdot \sqrt{2\pi}} \cdot \int_{E_m-3\sigma}^{E_m+3\sigma} G(E, T) dE \quad (3.33)$$

The equation (3.33) can be broken down into:

$$G(E, T) = \begin{vmatrix} G(E_m - 3\sigma, T_0) & G(E_m - 3\sigma, T_0 + \Delta T) & \cdots & \cdots & G(E_m - 3\sigma, T_0 + n\Delta T) \\ G(E_m - 3\sigma + \Delta E, T_0) & & & & \vdots \\ \vdots & & & & \vdots \\ \vdots & & & & \vdots \\ G(E_m + 3\sigma, T_0) & G(E_m + 3\sigma, T_0 + \Delta T) & \cdots & \cdots & G(E_m + 3\sigma, T_0 + n\Delta T) \end{vmatrix} \quad (3.34)$$

where $T = T_0, T_0 + \Delta T, T_0 + 2\Delta T, T_0 + 3\Delta T, \dots, T_n = T_0 + n\Delta T, E_m - 3\sigma < E < E_m + 3\sigma$.

Note that total number of terms in the $\mathbf{G}$ matrix will increase as the temperature T is increased or as ΔT is reduced. The value for B was set at 1.67×10^{13} [1/s] from transition state theory (Anthony et al., 1973). Assuming E_m and σ , volatile mass fraction $\{m_v(T)/m_{v,0}\}$ can now be calculated at a selected T by using $G(E, T)$ in equation (3.33). Let the error between the calculated and measured $m_v(T)/m_{v,0}$ from TGA be ε_j at selected $T = T_j$. The values for E_m and σ were calculated by minimizing the summed squared error $\sum_j \varepsilon_j^2$ at all selected data points within the domain of pyrolysis.

A spread sheet program was developed to determine the values of E_m and σ for the minimum most $\sum_j \varepsilon_j^2$. In the spread sheet, first the value of E_m is fixed and σ is varied. For a fixed value of E_m , there is a value of sigma that will produce the minimum amount of error $\sum_j \varepsilon_j^2$. Then E_m is varied and the combination of E_m and σ that produces the minimum most error can be determined.

3.8 CHEMICAL KINETICS

3.8.1 Activation energy from single reaction model

The activation energies of five different biomasses, Low ash raw manure (LARM), low ash partially composted manure (LAPC), high ash raw manure (HARM), high ash partially composted manure (HAPC), and Texas Lignite coal (TXL), were determined by using the single reaction model. Tests were performed to see the variation of activation energy with changes in volatile matter (VM) of the fuel and mean particle diameter. Five fuel types were tested in a thermo gravimetric analyzer. Tests were conducted on three particle sizes: as received, 75 μm , and 45 μm . The activation energy for each of the fuels from the single reaction model is shown in Figure 3.17. The results indicate that the activation energy for low ash biomass is higher than that of high ash biomass for both raw and partially composted samples. In addition, the raw manure samples have slightly higher activation energies than the partially composted samples. It is noted that a uniform

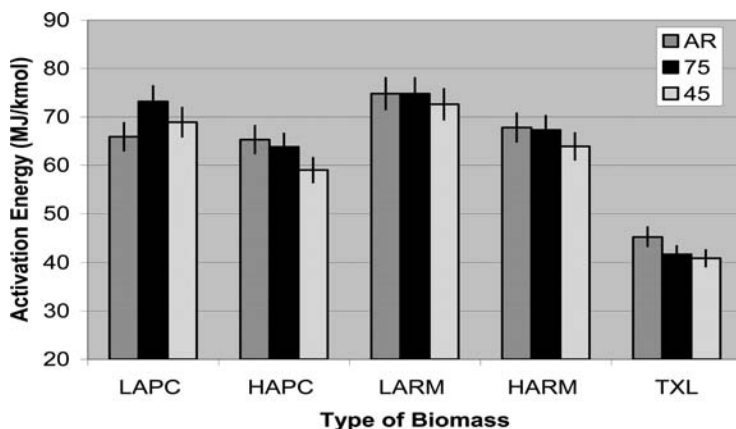


Figure 3.17. Activation energy results obtained using the single reaction model (adopted from Martin, 2006): AR: as received, 75 microns and 45 microns, $B = 1.67 \times 10^{13}$ 1/s. LARM: Low ash raw manure, HAPC: High ash partially composted manure, LARM: low ash raw manner, HARM: high ash raw manure, TXL: Texas Lignite coal.

Table 3.5. Activation energies from parallel reaction energy model, adopted from Martin (2006); $B = 1.67 \times 10^{13}$ 1/s.

Fuel	Parallel reaction model (KJ/kmol)
Dairy biomass	61316
Sorghum	129548
LARM	169000
LAPC	175000
HARM	172000
HAPC	173000
TXL	22500

particle temperature assumption has been used. The size effect on pyrolysis values comes through the temperature gradient within the particle; however, the particle sizes here are extremely small. In addition, the heating rates are low; thus, the size effect may not be responsible for different activation energies.

3.8.2 Activation energies from parallel reaction model

By applying a parallel reaction model the activation energies of different types fuel such as DB, sorghum, LARM, LAPC, HARM, HAPC, and TXL can be determined (as Table 3.5).

3.9 IGNITION

3.9.1 Ignition temperature

TGA analysis can also be used to determine the ignition temperature of a fuel when experiments are performed in an air environment. Each fuel was first analyzed in a nitrogen environment and then analyzed again in an air environment. The TGA traces of the two fuels began similarly, but upon ignition, the fuel would oxidize if air was present. Ignition caused the two TGA traces to

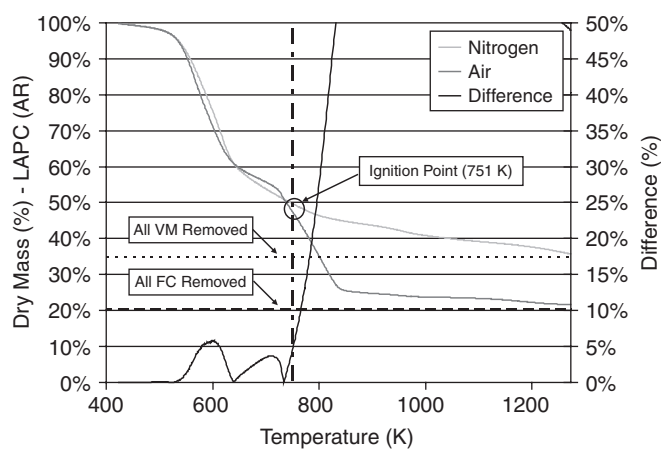


Figure 3.18. Dry mass vs. temperature with ignition point definition (adopted from Martin, 2006).

Table 3.6. Ignition temperature for various FB samples (Martin, 2006); blend ratio: coal biomass.

Particle size:		AR	75	45			AR	75	45
Fuel	Blend ratio	All temperatures are in degrees Kelvin			Fuel	Blend ratio	All temperatures are in degrees Kelvin		
LAPC	100-0	574	543	566	LARM	100-0	574	543	566
	90-10	568	540	536		90-10	561	557	549
	70-30	580	562	555		70-30	591	573	544
	50-50	572	560	549		50-50	571	565	569
	0-100	751	752	742		0-100	755	728	746
HAPC	100-0	574	543	566	HARM	100-0	574	543	566
	90-10	603	565	550		90-10	581	567	540
	70-30	595	573	556		70-30	565	569	560
	50-50	604	594	570		50-50	591	576	562
	0-100	733	774	787		0-100	715	757	726

deviate. The temperature at which this deviation occurred was defined as the ignition temperature (Fig. 3.18). For the mass loss traces obtained during testing, ignition is defined as the point at which the difference between the moisture normalized traces begin to deviate by more than 5% of the average value at that point and continue to deviate thereafter (Lawrence, 2007):

$$\left[\frac{(m\%)_{N_2} - (m\%)_{air}}{(m\%)_{N_2} + (m\%)_{air}} \right] > 5\%$$

This is best illustrated graphically as in Figure 3.18.

The ignition behavior of the biomass fuels was analyzed with similar independent variables as those used to analyze the activation energy behavior (Table 3.6). Figure 3.18 gives the temperature [K] at which ignition of the fuel sample is said to have occurred according to the definition.

The results show that the fixed carbon content of the fuel, particle size, and coal: FB blend ratio had very little effect on the ignition temperature of the fuel. The fixed carbon content for all the fuels tested is given in Table 3.7.

Table 3.7. Fixed carbon comparison for various FB samples.

Fuel		HAPC	LAPC	HARM	LARM
Coal present	FB present	% Fixed carbon as received basis			
100%	0%	25.41	25.41	25.41	25.41
90%	10%	23.21	24.02	23.47	24.08
70%	30%	18.80	21.25	19.59	21.43
50%	50%	14.39	18.47	15.71	18.78
0%	100%	3.36	11.54	6.02	12.16

Table 3.8. Higher heat value of fuels and volatile matter from parent fuel.

Fuel	Chem. formula	HHV-DAF, kJ/kg	VM-DAF %	HHV of VM* kJ/kg	Ref
Wy coal	CH _{0.71} N _{0.014} O _{0.18} S _{0.0014}	29805	46.7	26430	Thien <i>et al.</i> (2012)
TX lignite	CH _{0.68} N _{0.016} O _{0.19} S _{0.0061}	28460	49.4	25650	Thien <i>et al.</i> (2012)
LA PC feedlot biomass (FB)	CH _{1.28} N _{0.05} O _{0.53} S _{0.0056}	21370	81.9	18130	Arumugam <i>et al.</i> (2009)
LAPCDB	CH _{1.25} N _{0.047} O _{0.40} S _{0.0046}	21450	78.3	18310	Lawrence <i>et al.</i> (2009)
Litter biomass, LB	CH _{1.55} N _{0.091} O _{0.60} S _{0.0087}	19585	82.3	16750	Lawrence <i>et al.</i> (2009)
Mesquite	CH _{1.3582} N _{0.0122} O _{0.5779} S _{0.0003}	20128	79.82	16933	Chen <i>et al.</i> (2012)
Juniper	CH _{1.3708} N _{0.0049} O _{0.5637} S _{0.0001}	20584	84.55	18358	Chen <i>et al.</i> (2012)

*Computed from $HHV_{DAF} \approx VM_{DAF} * HHV_{VM} + FC_{DAF} * HV_{FC}$ where $HV_{FC} \approx 32765$ kJ/kg of carbon (Chapter 4, Annamalai and Puri, 2007).

Boie based HHV_{VM} in kJ/kg of VM released $\approx [35160Y_C + 116225Y_H - 11090Y_O + 6280Y_N + 10465Y_{SFC} * HV_{FC}]/VM]$, where VM, FC... $Y_C, Y_H, \dots$ are either in mass fractions as received or %.

The type of FB used also had little effect on the ignition behavior of the fuel. The overall average ignition temperature for those fuels, which had coal present, is 566 K with a standard deviation of only 2.9%. The only appreciable difference in ignition point temperature is for those fuels that were pure biomass. For the pure biomass fuels, no matter the particle size, the average ignition temperature is 747 K with a standard deviation of 2.7%, probably due to lower quality of volatiles from biomass fuels.

It can be seen from Table 3.8 that coal volatiles are of high quality compared to volatiles from biomass.

3.10 COFIRING

More recently, animal biomass has also been considered as a possible feedstock for smaller, on-the-farm combustion systems designed to properly dispose of animal solids and wastewater. Using commercially available equipment like solid separators, augers, and dryers, DB can be prepared for smaller combustion processes (Carlin *et al.*, 2007). A study by (Rodriguez *et al.*, 1998)

investigated the effect of drying on biomass heating values. Moreover, additional information on biomass fuel properties and heating values can be found in Annamalai and Puri (2007) and Annamalai *et al.* (1987). In the following sections of this chapter, the facilities and experimental work being conducted at the TAMU Department of Mechanical Engineering will be discussed.

It has been proposed that cattle biomass (CB) and litter biomass (LB) can be used as a fuel source for power generation. The CB includes both FB and DB. Previous attempts to use CB as a sole fuel source in gasifiers or direct combustion have resulted in limited technical success due to the high moisture content, high ash content, and/or low heating value of manure (Sweeten *et al.*, 2003). These properties which are found in most animal manure-based biofuels cause flame stability problems, and the high ash/soil content can clog conventional combustion devices and accelerate boiler tube erosion and corrosion. The more the volatile matter and lower the temperature at which volatiles are released, the better the flame stability in the boiler burner. Thus, co-firing biomass with coal may improve flame stability. FB, DB or LB could be used as a fuel by mixing it with coal and firing it in an existing coal suspension fired combustion system. This technique is known as co-firing. The high temperatures produced by the coal will allow the biomass to be completely combusted. If only 10% by mass LB is used, the fuel properties will not change radically, and few adjustments will have to be made to existing combustion system equipment. Previous boiler co-firing experiments involving biomass with pulverized coal have included: wood waste (Gold *et al.*, 1996), switch-grass (Aerts *et al.*, 1997), straw (Hansen *et al.*, 1998), sewage sludge, tire-derived refuse (Abbas *et al.*, 1994), or grass (Spliethoff *et al.*, 1998). Chapter 5 of this book deals with combustion of biomass fuels and various combustors used for energy conversion: pile, grate, fluidized beds, suspension burners (Desidiri and Fantozi, 2013).

The use of FB as a co-firing fuel was previously investigated by Frazzita *et al.* (1999) using a small-scale boiler burner to co-fire FB and coal under transient conditions. A lack of adequate insulation and steel combustor walls allowed the experiments to obtain only transient results at low temperatures. Additional co-firing experiments are summarized by Sami *et al.* (2001).

Figure 3.19 presents an overview of a number of co-firing plants in Europe. All together, there have been around 100 co-firing units in Europe. Co-firing plants in the Netherlands, Denmark, Finland and Sweden are mostly operating on a commercial basis while many of the plants in the UK are in trials or demonstrations. Positive experience in co-firing has been made mainly with woody biomass (EUBIA). There are different biomass employment methods for co-combustion and three main co-firing combustion methods (direct, indirect, parallel). Co-firing can be accomplished by different technologies like atmospheric or pressurized fluidized bed combustors, pulverized or grate combustors (EUBIA). The majority of the European co-fired power plants operate in direct co-combustion with circulated fluid bed boilers (EUBIA).

It is apparent from a literature review that there are no prior data on the effect of co-firing low quality and high nitrogen DB on the combustion and emission characteristics.

3.10.1 *Experimental set up and procedure*

All co-firing experiments were conducted using a 30 kW (100,000 BTU/h, approximately 15 lb or 6.80 kg of coal/h) small-scale furnace capable of firing most types of ground fuels. A schematic of the furnace is shown in Figure 3.20. Propane and natural gas are used to heat the furnace to the operating temperature of 1100°C (2000°F). Type K (shielded, ungrounded) thermocouples are used to measure the temperature along the axial length of the furnace. A solid fuel hopper feeds coal and coal/biomass blends during experiments. Primary air (6 m³/h, 15–20% of total air) is necessary to propel the finely ground solid fuel through the fuel line and to the furnace. Prior to ventilation, all exhaust gases pass through a water-cooling spray to significantly lower the temperature of the gases. A sump pump pumps this water out of the furnace. More details are provided in Frazzita *et al.* (1999), Arumugam *et al.* (2006c), Annamalai *et al.* (2005), Lawrence *et al.* (2009) and in Thien *et al.* (2012).

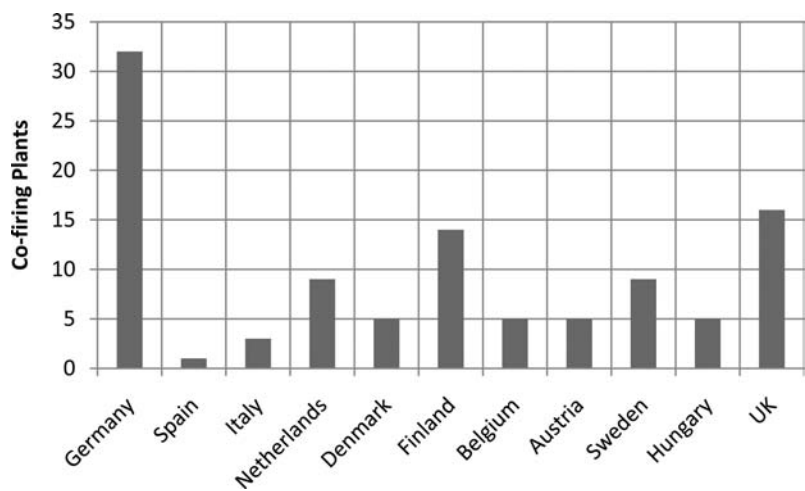


Figure 3.19. Co-firing power plants in Europe (adopted from European Biomass Industry Association (EUBIA)).

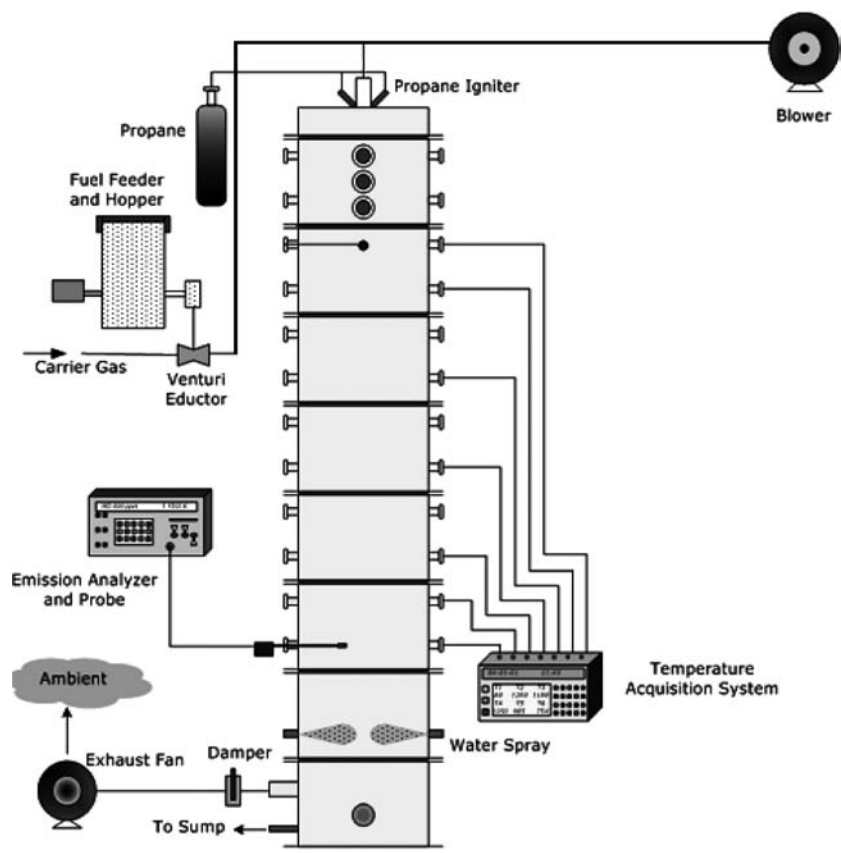


Figure 3.20. Schematic of boiler burner facility for co-firing (adapted from Lawrence, (2007)).

The secondary air (75–80% of total air) heater was run for an hour before the experiment was started. The secondary air is swirled (Swirl number = 0.7) prior to entry into the combustion chamber. Once the secondary air reached a steady temperature, approximately 500 K (440.33°F), the propane torches were ignited. Natural gas and propane were used to preheat the furnace to operating temperatures. Once the furnace reached 1366 K (2000°F), the natural gas was turned off and the natural gas line was closed. The solid feeder line was opened and the solid feeder was turned on and set to the desired fuel flow rate. The primary and secondary air lines were set to the appropriate flow rates to obtain the desired equivalence ratio. The furnace was allowed to run for 30 minutes before the first readings were taken. The measurement was taken at the last sampling port just before the quenching water sprays and the wet flue gases were ducted to the atmosphere. After taking a measurement at this equivalence ratio, the secondary air could be adjusted to a different equivalence ratio. After taking measurements at all desired equivalence ratios, the furnace was turned off.

Fuel properties played a significant impact on the burnt fraction and the emissions created by combustion. The results from the co-firing experiments performed are discussed and their role in evaluating the combustion performance of the fuels is explained. The performance was evaluated by measuring combustion efficiency (burnt fraction) and the emissions levels of pollutants that include NO_x and CO. In addition, overall fuel nitrogen conversion efficiency to NO_x was also determined. The mercury emissions are presented elsewhere (Udayasathy, 2007).

The co-firing involves a mix of finely pulverized biomass and coal. The size distribution was obtained using an ASTM sieve shaker. Sauter mean diameter (commonly abbreviated as *SMD* or d_{32}) is commonly used for estimating the average size of solid fuel particles. The *SMD* is defined as the diameter of a sphere that has the same ratio of volume to surface area. It is represented as the following equation:

$$\text{SMD or } d_{32} = \frac{\sum_{i=1}^n d_i^3 \cdot n_i}{\sum_{i=1}^n d_i^2 \cdot n_i}$$

where d_i is the diameter of particles and n_i is the number of the particles of diameter d_i . According to the Rosin Rammler fit, the cumulative mass fraction *CMF* or drops (or particles) with a dimension lesser than d_p is given as (Annamalai and Puri, 2007):

$$\text{CMF} = 1 - \exp(-bd_p^n)$$

where b : size constant, n : distribution constant and is a measure of spread of drop size. In terms of the $d_{p, \text{charac}}$ size:

$$\text{CMF} = 1 - \exp\left(-\frac{d_p}{d_{p, \text{charac}}}\right)^n$$

where $d_{p, \text{charac}}$ denotes the characteristic drop or particle size for which $\text{CMF} = 1 - \exp(-1) = 63.2\%$ and

$$b = \left(\frac{1}{d_{p, \text{charac}}^n}\right)$$

The fraction R having size greater than d_p is:

$$R = 1 - \text{CMF} = \exp\left(-\frac{d_p}{d_{p, \text{charac}}}\right)^n$$

The plot of $\ln\{R\}$ vs. d_p must be linear and the slope yields “ n ” and $d_{p, \text{charac}}$ is determined from the plot at $R = 0.368$. The values of “ n ”, “ b ” and *SMD* are presented in Table 3.9 for several fuels. Note that the coals had a larger *SMD* than those of DB fuels. The dirt (or mineral matter) that got collected with the DB fuels passed through all of the sieves and collected in the pan. This caused the DBs to have a smaller *SMD*.

Table 3.9. Size distribution parameters, adopted from Lawrence (2007).

Size distribution parameters				
	TXL	WYO	LA-PC-DB-SepS	HA-PC-DB-SoilS
n	1.2991	1.4369	1.0934	1.2612
b	0.000934	0.00042	0.0024	0.0013
SMD (microns)	396	396	96.7	91.6

3.10.2 Experimental parameters

TXL was used as the base case fuel. TXL and WYO were fired as blends with two DB fuels. Each coal was blended with each DB fuel in 100-0, 95-5, 90-10, and 80-20 blends on a mass basis. Note that on a heat basis, the percent of heat attributed to each fuel type was much less compared to percent mass basis. For example: for the 80:20 WYO:HA-PC-DB-SoilS fuel, 80% of the mass was WYO, but more than 94% of the heat came from WYO. All fuel and air flow rates were calculated from a program developed by Goughnour (2006). For each blended fuel, the equivalence ratio was varied from 0.8 to 1.2 in 0.1 increments. Combustion any leaner than 0.8 created a heavy strain on the compressor and was also useless for industrial applications. The 80-20 blends were too rich in DB to be used in industrial applications, but were used in order to get more data points for the study. In the rich regime (equivalence ratio > 1.0) the HA-PC-DB-SoilS (Fig. 3.3b) quickly clogged the sampling port due to high ash content and may not be suitable for co-firing with coal; however it could be used as fuel for producing low heat value gases using gasifiers (see the section on gasification). The coal: biomass blends needed slightly more fuel flow rates compared to pure coal in order to compensate for the lower energy content of biomass for same thermal output.

3.10.3 O_2 and equivalence ratio

The air fuel ratio, and hence the equivalence ratio, can be estimated from measured flow rates of air and fuel. It can also be computed using the measured O_2 percentage in the exhaust for lean mixtures. Using O_2 percentage data the equivalence ratio of the exhaust stream was approximated by:

$$\varphi_{flue} \approx 1 - 4.76 * O_2, \quad \varphi_{flue} < 1.0 \quad (\text{Annamalai and Puri, 2007})$$

The equation above assumes that all the fuel has been gasified. If large particles are not gasified, the O_2 percentage will increase. This will cause the φ based on exhaust gases to decrease. Figure 3.21 plots the φ_{flue} computed from flue gas analysis *versus* the φ_{flow} computed from air and fuel flow rates. It is seen that φ_{flue} is less than φ_{flow} . This indicates that the burnt fraction (BF) BF is less than 1.0. Also, note that the φ_{flow} requires knowledge of the fuel flow rate. Due to limitations of the feeder, only average flow rates of solids could be measured. Figure 3.22 presents the exhaust equivalence ratio for WYO and WYO:DB blended fuels. Ideally, the data points would follow the ideal line ($\varphi_{flue} = \varphi_{flow}$). The real data points lie within the experimental uncertainty of each other. This indicates that the values are valid. In all future plots, the φ represents the equivalence ratio based on measured air flow rates and the calibrated fuel flow rate.

3.10.4 CO and CO_2 emissions

Figure 3.23 and Figure 3.24 present the CO_2 and CO exhaust concentrations for TXL and TXL:DB blended fuels, respectively. Very little CO was formed in the lean regime. In lean combustion, there

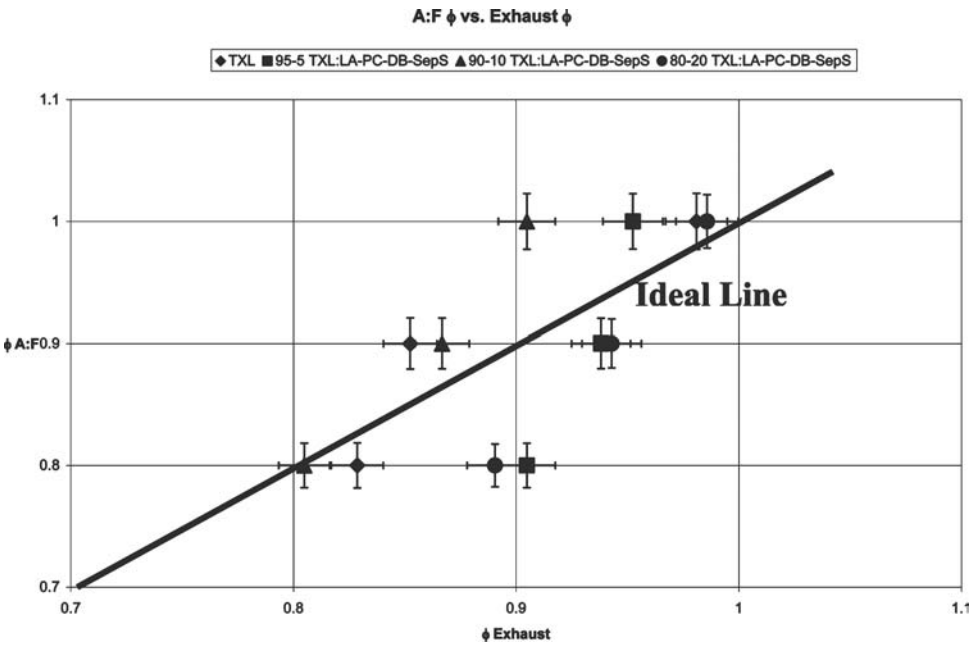


Figure 3.21. Equivalence ratio based on air flow rates ($\phi_{A:F}$ is same as ϕ_{flow}) and the calibrated fuel flow rate vs. equivalence ratio based on $\text{O}_2\%$ in exhaust for TXL and TXL:DB blended fuels (adopted from Lawrence, 2007).

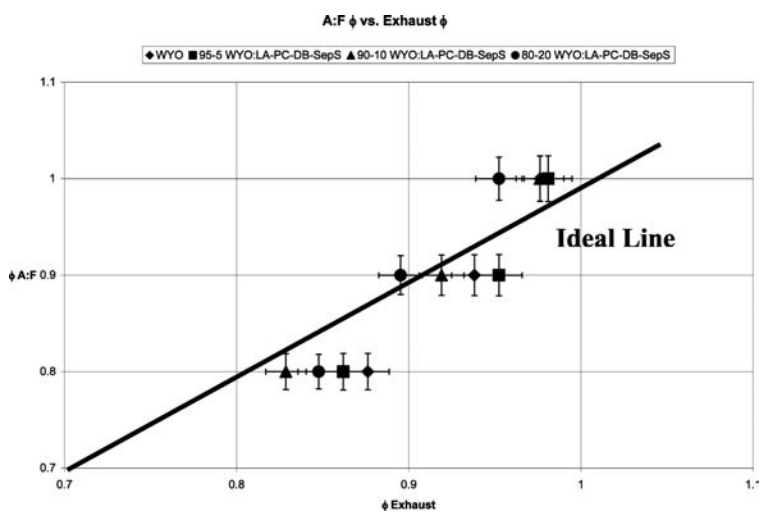


Figure 3.22. Equivalence ratio based on air flow rates ($\phi_{A:F}$ is same as ϕ_{flow}) and calibrated fuel flow rate vs. equivalence ratio based on $\text{O}_2\%$ in exhaust for WYO and WYO:DB blended fuels (adopted from Lawrence, 2007).

is sufficient oxygen for all the carbon to fully oxidize to CO_2 . However, once combustion became oxygen deficient CO begins to be formed. In general, the blended fuels produced more CO because the DB fuels contained more oxygen and they release more CO during pyrolysis.

The equivalence ratio was based upon measured air and calibrated fuel flow rates. It is apparent that CO_2 peaked at approximately the stoichiometric condition. As air flow was increased from

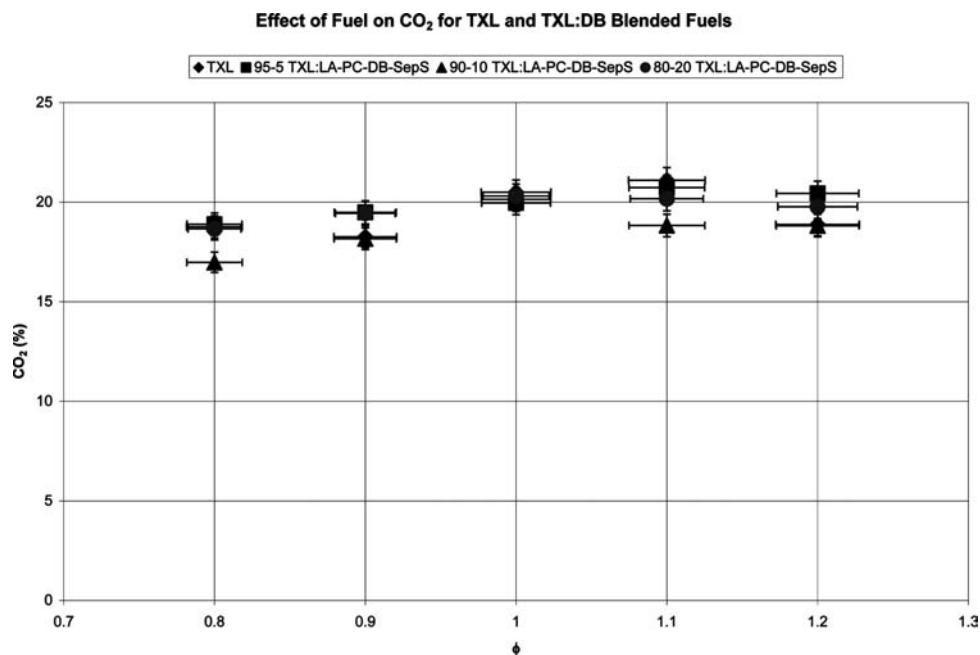


Figure 3.23. Effect of fuel on CO₂ for TXL and TXL:DB blended fuels (adopted from Lawrence, 2007).

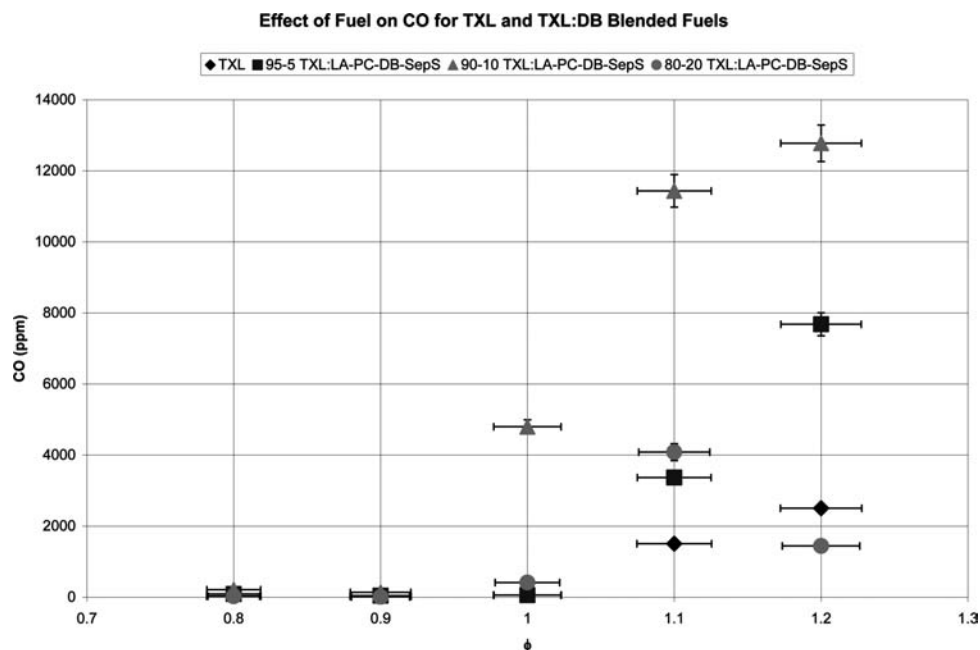


Figure 3.24. Effect of fuel on CO for TXL and TXL:DB blended fuels (adopted from Lawrence, 2007).

the stoichiometric point, the excess air diluted the flue gas concentrations. This dilution effect decreased the CO₂ percentage. On the other hand, if air flow was decreased below the stoichiometric air flow rate, less CO₂ was formed due to insufficient O₂ to oxidize fuel-bound carbon. This explains why the peak in CO₂ was at approximately stoichiometric.

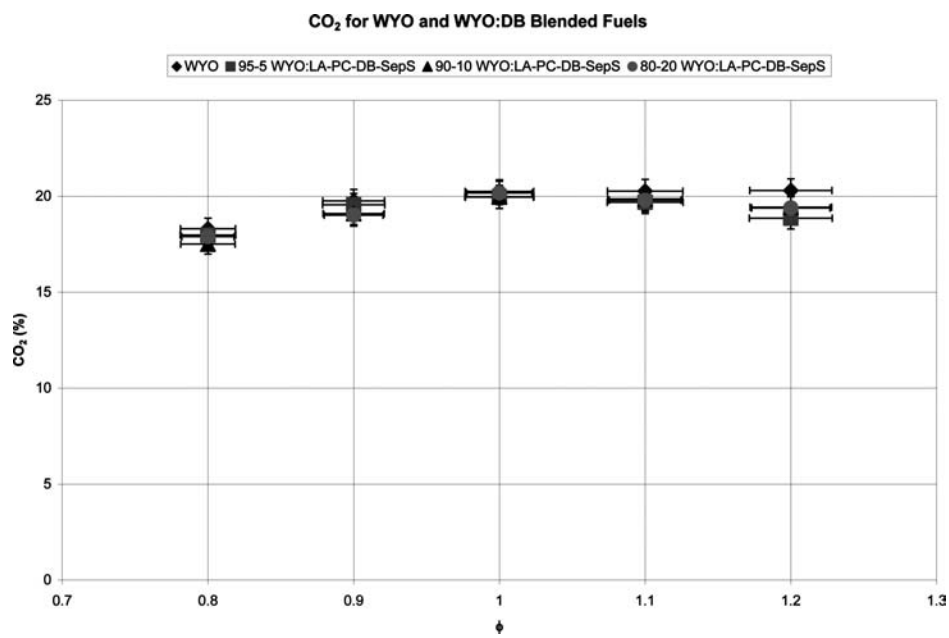


Figure 3.25. Effect of fuel on CO₂ for WYO and WYO:DB blended fuels (adopted from Lawrence, 2007).

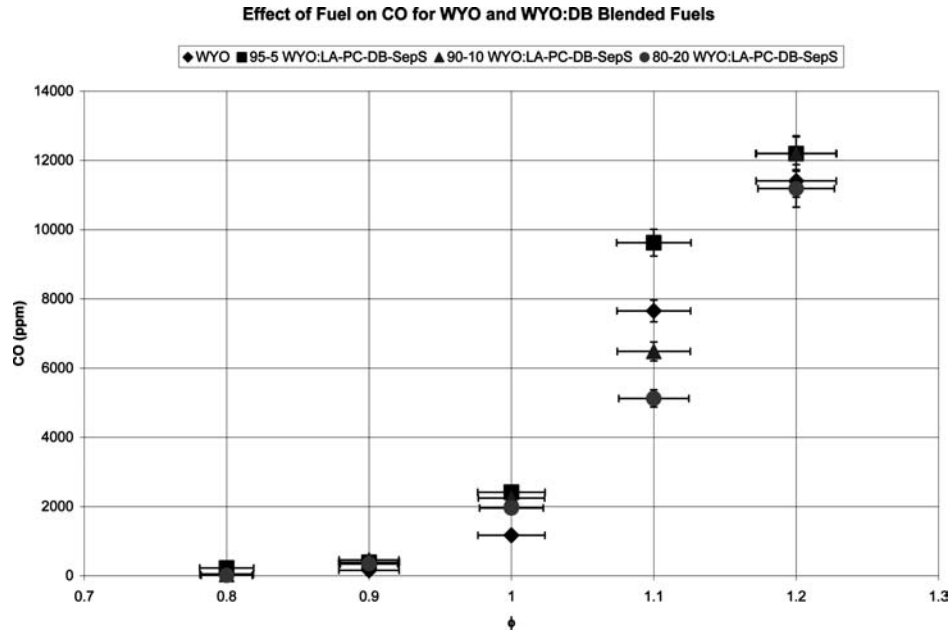


Figure 3.26. Effect of fuel on CO for WYO and WYO:DB blended fuels (adopted from Lawrence, 2007).

WYO presented trends similar to those of TXL:DB blends. Figure 3.25 and Figure 3.26 present the CO₂ and CO concentrations for WYO and WYO:DB blended fuels. The wider uncertainty bands for CO were due to the uncertainty in CO measurements being a percentage of the reading. The uncertainty bands overlap too much to draw any conclusions about the effect of blending coal with DB on CO production. The equivalence ratio was based upon air and fuel flow rates.

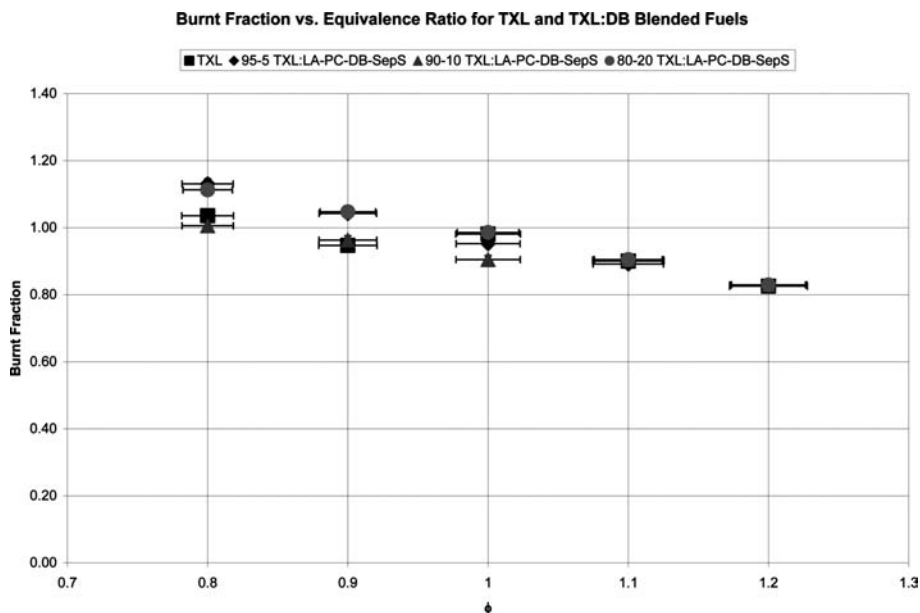


Figure 3.27. Effect of fuel on BF for TXL and TXL:DB blended fuels. Note that in the rich regime, the BF overlaps for all fuels. This indicates that the same percentage of all fuels was burnt (adopted from Lawrence, 2007).

3.10.5 Burnt fraction

Recall that O_2 in the exhaust is an indicator of φ used in experimentation. Thien (2002) derived an expression for the burnt fraction of a solid fuel approximated as:

$$BF \approx \frac{1}{\varphi} * \left(1 - \frac{X_{O_2}}{X_{O_{2,A}}} \right);$$

where BF is the burnt fraction, φ is the measured equivalence ratio from flow rates, X_{O_2} is the mole fraction of oxygen in the exhaust gases (dry basis), and $X_{O_{2,A}}$ is the mole fraction of oxygen in the ambient air (dry basis). This equation can be used for rich or lean mixtures. When BF is very high, near unity, it implies that all of the fuel was combusted. Note that BF is larger than 1 for some of the extremely lean experiments. These values demonstrate the limitations of equation (3.2) as well as experimental uncertainties including fuel compositions. As is to be expected, BF decreased with increasing equivalence ratio. In rich combustion, insufficient air was provided to completely oxidize all fuel carbon to CO_2 , leaving unburned fuel in the ash. This caused the BF to be less than 1.

Figure 3.27 and Figure 3.28 present the BF for TXL and TXL:DB blended fuels and WYO and WYO:DB blended fuels, respectively. Even in the very rich combustion ($\varphi = 1.2$), approximately 83% of the fuel was burnt.

3.10.6 NO_x emissions

As the temperature of the reactor is insufficient to generate thermal NO , the source of NO is fuel nitrogen. Thus most NO comes from oxidation of fuel N. Correcting the NO emissions of 3% O_2 is a common industry practice to prevent utilities from artificially diluting NO_x emissions with O_2 . In the very lean regime, correcting caused the NO_x emissions to increase. However, for

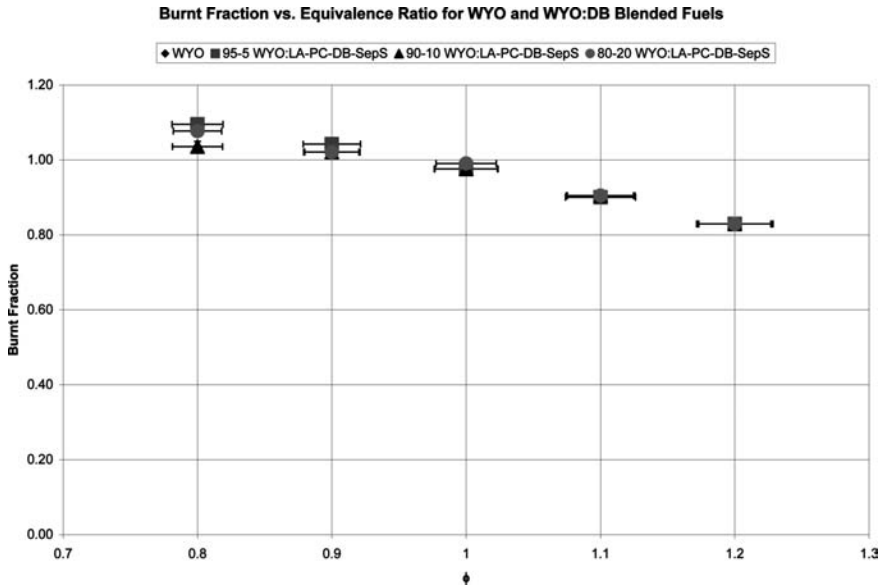


Figure 3.28. Effect of fuel on BF for WYO and WYO:DB blended fuels. Note that the data points come close to overlapping for all equivalence ratios. Thus, BF was independent of fuel type (adopted from Lawrence, 2007).

all other equivalence ratios, correcting caused the NO_x emissions to decrease because there is less than 3% O_2 in the exhaust prior to correcting. Figure 3.29 and Figure 3.30 present the NO_x emissions for TXL and TXL:DB blended fuels in ppm and corrected to 3% O_2 . With the exception of 95-5 TXL:HA-PC-DB-SoilS, all of the blended fuels produced more NO_x in the lean region than the pure TXL even though DB contains more N. There are three possible reasons: (i) higher amount of fuel-bound nitrogen present in the biomass binding with the excess oxygen to form NO_x , (ii) release of more N in the form of NH_3 due to high urea in DB, and (iii) depletion of oxygen due to oxidation of higher amount of VM released at lower temperatures from biomass thus preventing the oxygen from bonding with fuel nitrogen.

Instead of reporting NO at 3% O_2 , another method employed to prevent emission dilution is to report NO_x levels on a heat basis. Annamalai and Puri (2007) presented the conversion formula from ppm of pollutant species k to k in kg/GJ, given that the fuel fired is $\text{C}_c\text{H}_h\text{O}_o\text{N}_n\text{S}_s$. For pollutant species k :

$$k \text{ [kg/GJ]} = \frac{cX_k}{(X_{\text{CO}_2} + X_{\text{CO}})} \frac{M_k}{M_F \text{HHV}_F \text{ [GJ/kg]}} \quad (3.35)$$

on an atom basis, where c is the carbon atoms in the fuel, X_k mole fraction of species k and M_F is the molecular weight of the empirical formula for the fuel. With $k = \text{NO}$:

$$\text{NO [kg/GJ]} = \frac{cX_{\text{NO}}}{(X_{\text{CO}_2} + X_{\text{CO}})} \frac{M_{\text{NO}_2}}{M_F \text{HHV}_F \text{ [GJ/kg]}} \quad (3.36)$$

where the molecular weight for NO is expressed in terms of the molecular weight of NO_2 , as required by the EPA. Figure 3.31 presents the NO_x emissions in kg/GJ of heat input.

Note that in the lean region, the blended fuels produce more NO_x than the pure WYO. In the slightly rich region, the blended fuels produce less NO_x than the pure WYO due to more release of N in the form of NH_3 from DB.

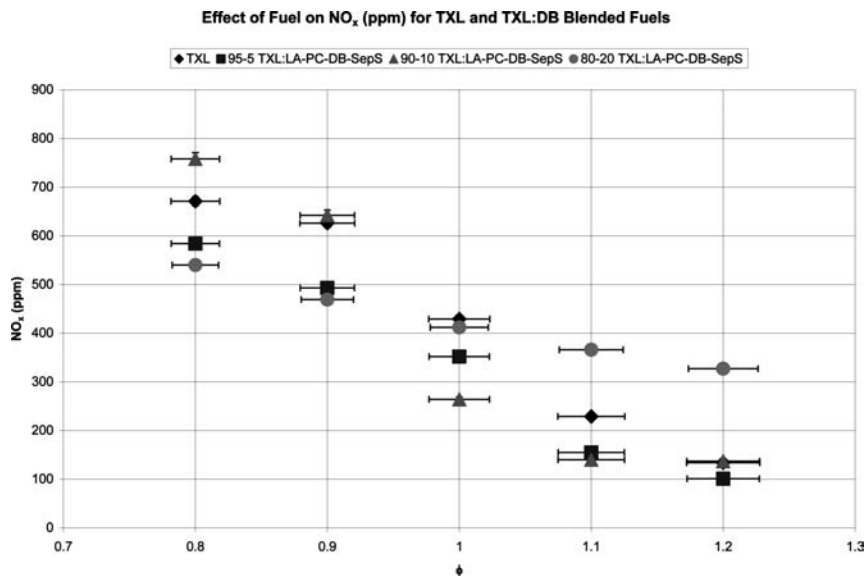


Figure 3.29. Effect of fuel on NO_x for TXL and TXL:DB blended fuels. Note that blended fuels have lower NO_x values at stoichiometric and in rich combustion (adopted from Lawrence, 2007).

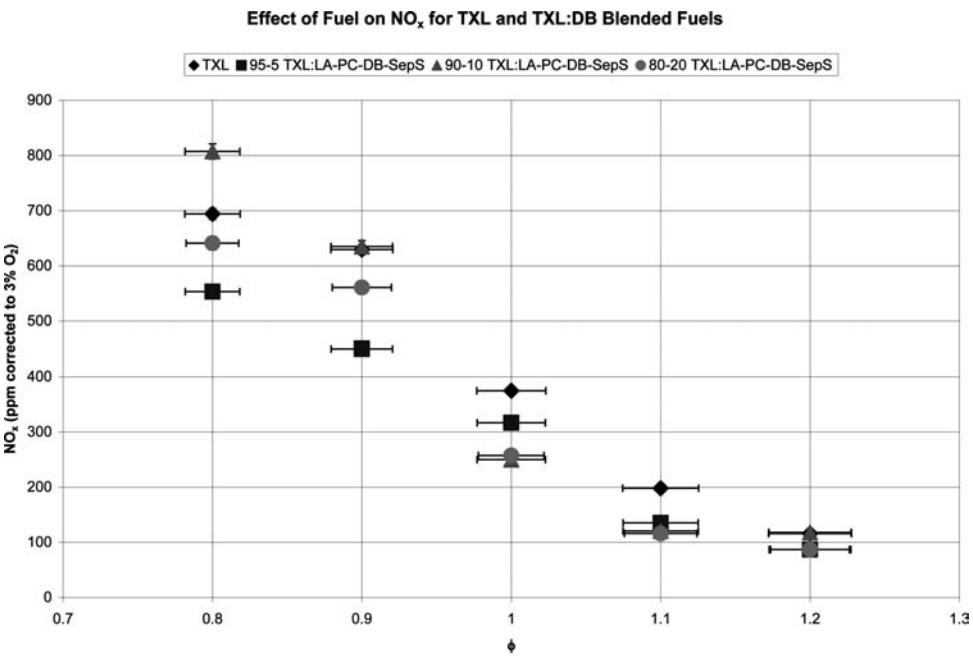


Figure 3.30. Effect of fuel on NO_x for TXL and TXL:DB blended fuels corrected to 3% O₂ (adopted from Lawrence, 2007).

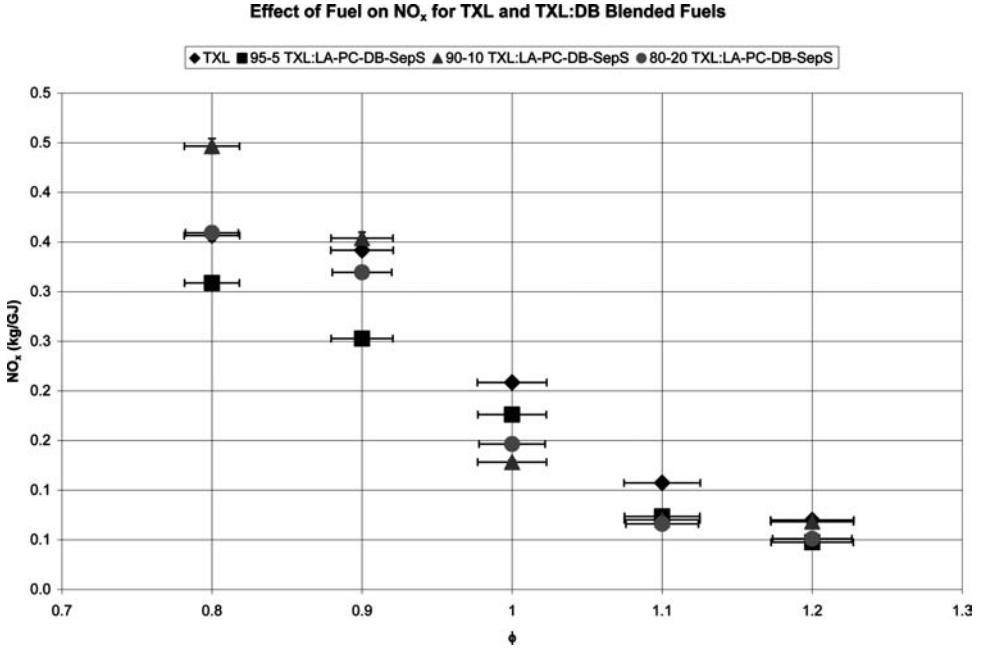


Figure 3.31. Effect of fuel on NO_x for TXL and TXL:DB blended fuels in kg/GJ (adopted from Lawrence, 2007).

The same explanation for TXL applies to the WYO fuels. Figure 3.32 and Figure 3.33 present the NO_x emissions from WYO and WYO:DB blended fuels in ppm and corrected to 3% O_2 . Figure 3.34 presents the NO_x emissions from WYO and WYO:DB blended fuels in kg/GJ of heat input.

3.10.7 Fuel nitrogen conversion efficiency

During combustion, only a fraction of fuel N is converted into NO_x (about 20% to 30% in sub-bituminous coal (Bowman, 1991, 2001)), while the remaining fuel N is released as N_2 with the flue gases. The reaction of N with oxygen is inhibited by carbon radicals bonding with available oxygen to form CO and CO_2 . The nitrogen conversion efficiency is defined as the amount of fuel nitrogen that gets converted to NO_x . Annamalai and Puri (2007) showed that overall fuel nitrogen conversion efficiency can be approximated by:

$$N_{CONV} \approx \frac{(c/n) * X_{\text{NO}}}{X_{\text{CO}_2} + X_{\text{CO}}} \quad (3.37)$$

where c/n is the atom ratio of the empirical carbon and nitrogen respectively, X_{NO} is the mole fraction of NO_x , X_{CO_2} is the mole fraction of CO_2 , and X_{CO} is the mole fraction of CO. All gases were measured in the exhaust stream. Note that the equation assumes that all NO_x originates from fuel nitrogen and hence it presents an upper bound on fuel nitrogen conversion efficiency. In addition, when fuel nitrogen conversion efficiency is very low, it means that most fuel-bound nitrogen is converted to something other than NO_x .

Note that as the equivalence ratio increased, less nitrogen was converted to NO_x . In the extremely rich region, the conversion efficiency was nearly 0%. The largest decrease in conversion occurred when the flame went from stoichiometric to rich. Figure 3.35 presents the fuel nitrogen conversion efficiency for TXL and TXL:DB blended fuels. Also note that in general, the

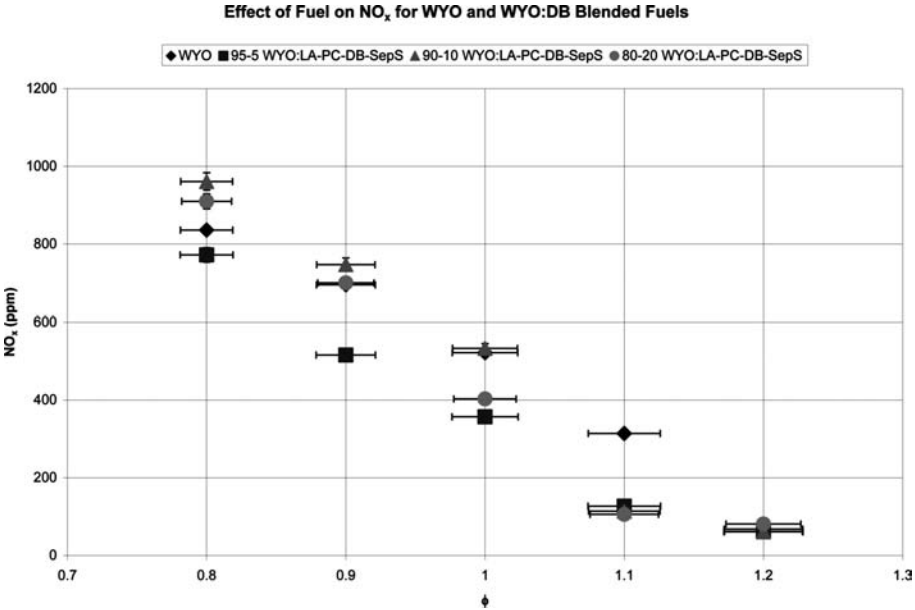


Figure 3.32. Effect of fuel on NO_x for WYO and WYO:DB blended fuels. Note how NO_x decreases in the near lean region for blended fuels (adopted from Lawrence, 2007).

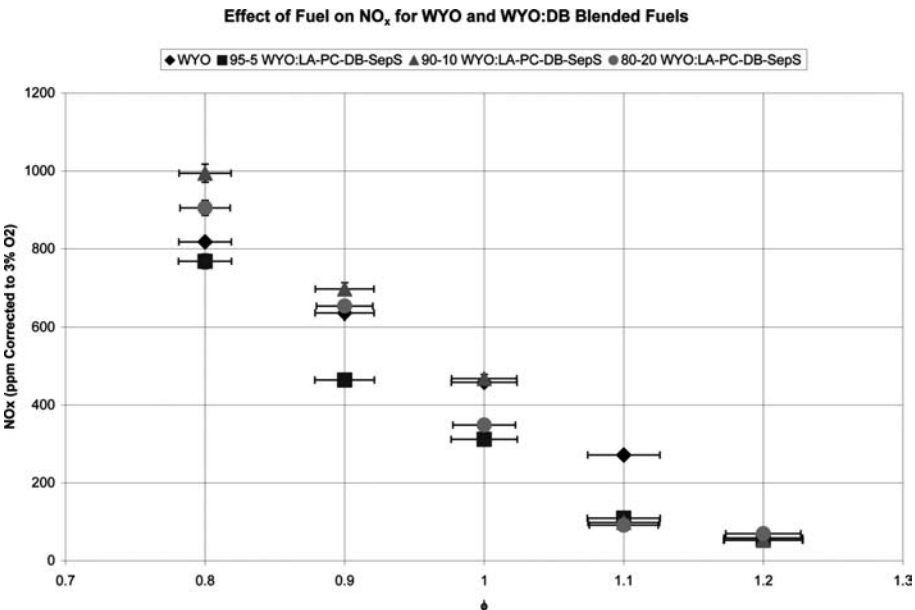


Figure 3.33. Effect of fuel on NO_x for WYO and WYO:DB blended fuels corrected to 3% O₂ (adopted from Lawrence, 2007).

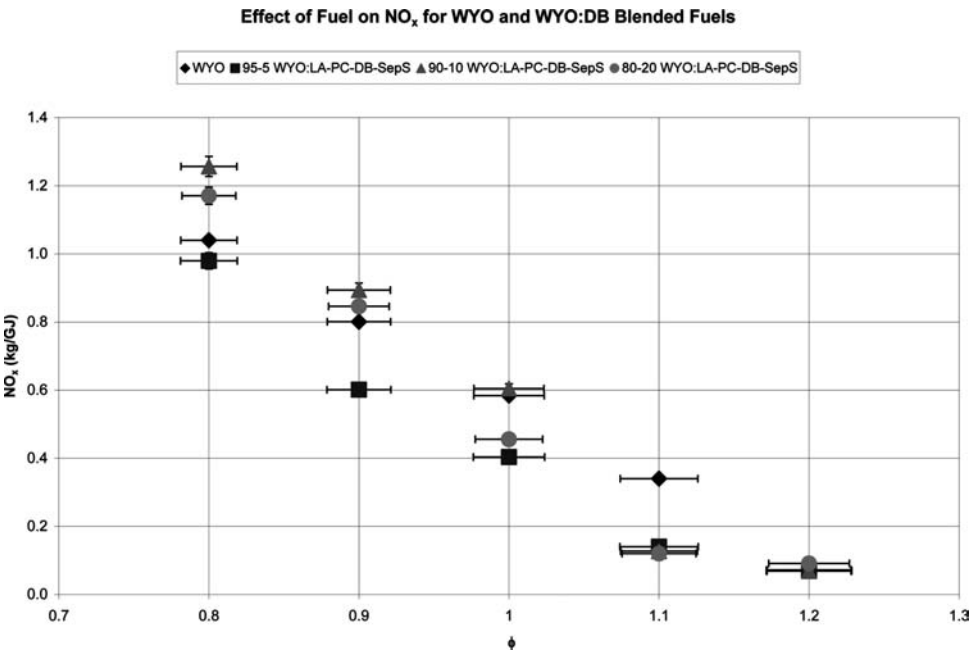


Figure 3.34. Effect of fuel on NO_x for WYO and WYO:DB blended fuels in kg/GJ (adopted from Lawrence, 2007).

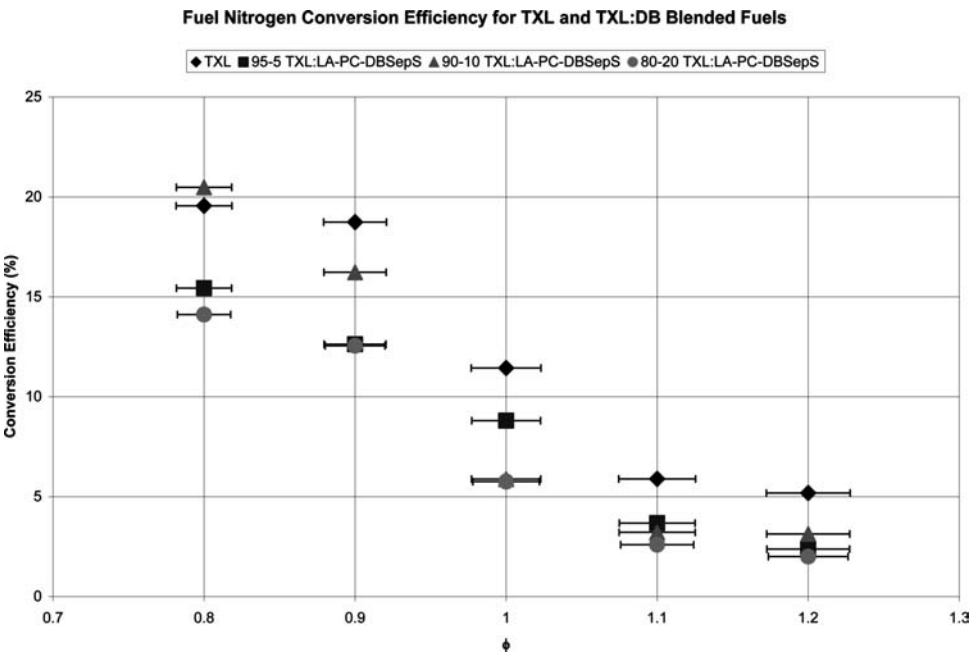


Figure 3.35. Effect of fuel on nitrogen conversion efficiency for TXL and TXL:DB blended fuels. Note that the conversion efficiency is less than coal for almost all TXL:DB blended fuels (adopted from Lawrence, 2007).

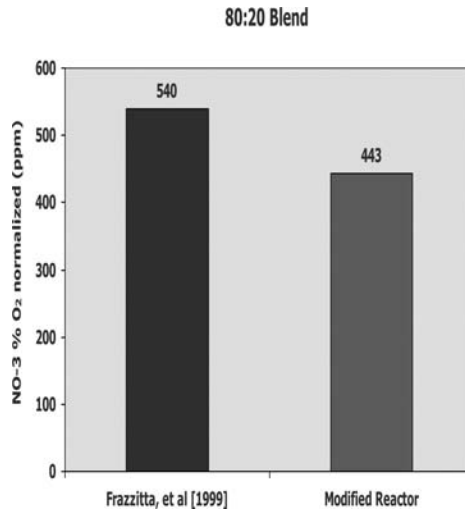


Figure 3.36. Effect of reactor length on NO emissions (adopted from Arumugam *et al.*, 2005). Modified reactor: length is longer.

DB blended fuels converted less nitrogen to NO_x . The same trend was observed with WYO and WYO:DB blended fuels.

As with NO_x reduction for AgB and coal blends, (section, 3.4.1), it is hypothesized that the increased volatile matter of AnB under co-firing conditions resulted in the increase of fuel N loading, greater depletion of O_2 and sometimes even in reduction in NO_x (Arumugam *et al.*, 2005). However, the increased fuel N in AnB produces more NH_3 due to urea type N in AnB. Thus, more NH_3 type species are produced in blend coal:AnB fuels. Under appropriate temperature and oxygen concentration, the NO_x reduction due to $\text{NH}_3 + \text{NO}_x$ reactions may dominate the reduction process of NO_x .

3.11 COFIRING FB WITH COAL

Additional literature concerned with co-firing FB with coal may be found in papers by Annamalai *et al.* (2007a, 2007b), Sweeten *et al.* (2003), Frazzitta *et al.* (1999), Arumugam *et al.* (2005), Annamalai *et al.* (2003) and Annamalai *et al.* (2003b). However, most co-firing experimental results with FB seem to indicate that NO_x emissions did not increase and sometimes even decreased. Therefore, it is hypothesized that FB may also be used in reburning facilities to both partially supplement coal and to reduce NO_x emissions.

3.11.1 NO emissions with longer reactor

The comparison of the NO measurements normalized to 3% O_2 in the exhaust with that of Frazzitta *et al.* (1999) is given in Figure 3.36. The measurements are depicted for the co-firing of 80:20 coal:FB blend with a 97% burnt fraction. Under both study conditions, a similar fuel N conversion efficiency of $\sim 16\%$ was observed. However, a lower NO value was measured as compared to the previous study, which might be attributed to the longer residence time available in the modified reactor. The residence time in the prior study was ~ 0.5 s at hot conditions as compared to ~ 1 s in the modified longer reactor. The higher duration available in the longer reactor aids the reduction of NO to further lower values. The increased residence times with modified reactor attributes 17% reduction in the normalized NO emission.

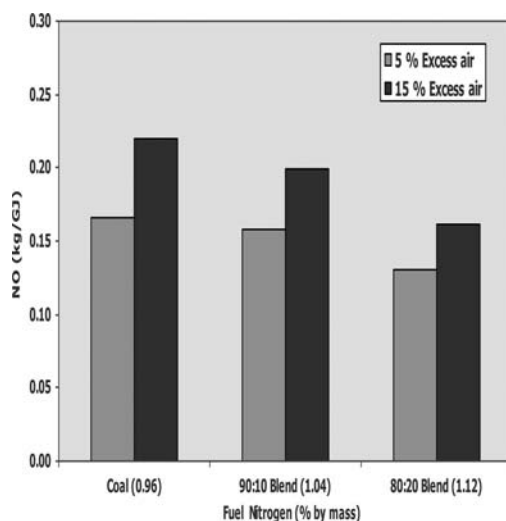


Figure 3.37. Variation of normalized exit NO emissions with fuel nitrogen content (adopted from Arumugam *et al.*, 2005).

3.11.2 Effect of blend ratio

A better understanding of the NO emissions can be observed when the fuel nitrogen content and the NO emitted are compared as shown in Figure 3.37. It can be observed that as the blend ratio is increased the fuel nitrogen content increases. Thus one would expect the formation of fuel NO to increase as the blend ratio is increased. On the contrary, the NO generated decreases. In the situation where the NO formation is only through fuel nitrogen, it is remarkable to observe that increasing FB content in cofired fuel does not necessarily lead to higher NO emissions. The trend is observed at different excess air ratios. Thus, the use of FB not only serves as a means of waste disposal, but also reduces the emissions. The reduction of NO_x with coal:FB blends is due to better grindability of FB compared to fibrous DB.

3.12 REBURN

Previous sections dealt with co-firing of FB and DB with coal in conventional boiler burners. In this approach, the high temperatures produced by the coal allow for the successful combustion of the FB. A 30 kW Boiler Burner Facility was built at Texas A&M and co-firing was performed which revealed better combustion of coal with FB and similar or less NO_x when cofired with coal even though FB has 2 and 4 times the N content of coal on a mass and heat basis. Small-scale co-firing tests were followed by pilot plant tests at the 500 kW facility of National Energy Technology Laboratory of DOE-Pittsburgh with similar results (Annamalai *et al.*, 2003b, 2003c). Further, the VM of CB on DAF basis was almost twice that of coal. The large amount of volatile content of the biomass in the blend consumes oxygen rapidly in the near-burner region, thereby creating more localized fuel-rich zones, and hence less NO is formed. In addition, it is believed that most of the N in FB exists as NH_3 , the volatile matter of FB is twice that of coal and hence NO_x emission did not increase. If so, the CB can serve as effective reburn fuel for NO_x reduction. A premixed propane and trace amounts of NH_3 were burnt to simulate coal combustion gases and use NH_3 to produce NO in the main burner, and then test coal and feedlot biomass as reburn fuel.

The experiments were conducted in the Texas A&M laboratory scale boiler burner that was modified for reburn experiments. The boiler is a 30 kW (100,000 Btu/h) downward-fired furnace

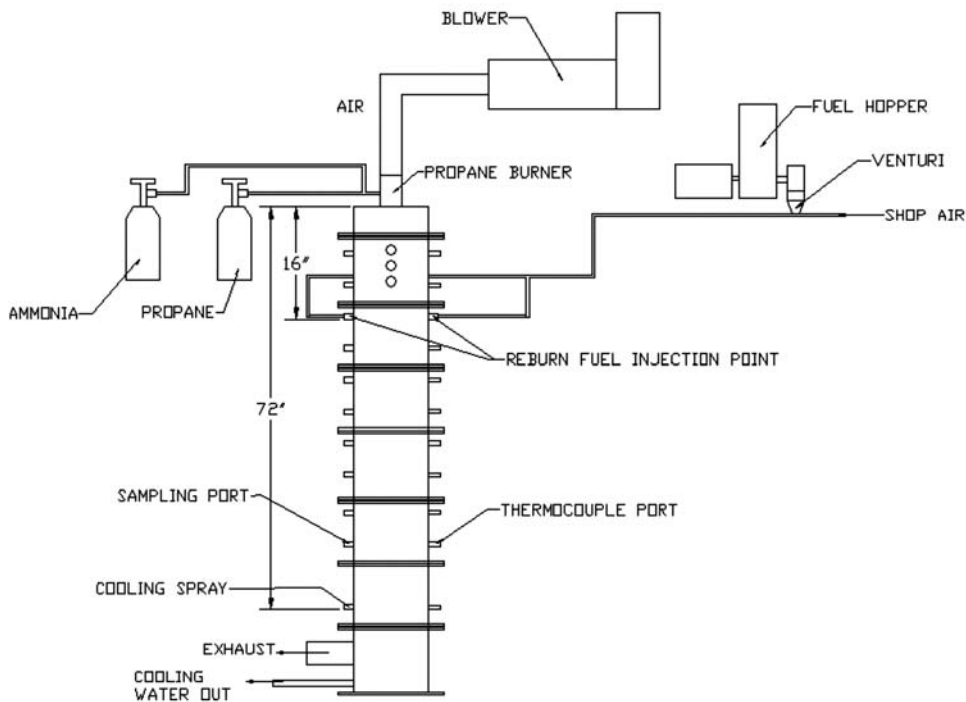


Figure 3.38. Experimental schematic for NO_x reduction with coal and FB blends (adopted from Annamalai and Thien, 2001).

made up of a steel shell encasing ceramic insulation. A schematic of the entire setup is shown in Figure 3.38. A premixed propane burner is mounted at the top of the furnace to produce hot furnace gases to simulate the products of coal combustion. Ammonia is injected into the premixed propane fuel stream and burnt in the primary zone. The primary or main burner zone equivalence ratio (ϕ_M) is typically < 1 indicating excess O_2 . The reburn fuel is fed from a dry solids feeder, through a venturi inductor valve, and injected through the reburn ports. The reburn injection ports are located below the tip of the premixed propane flame, after all of the NO has been formed in the primary zone. The reburn zone below the main burner receives excess O_2 left from the main burner and the O_2 from the reburn injector operated at equivalence ratio ϕ_{RB} . Thus the reburn zone equivalence ratio (ϕ_{RBZ}) is adjusted both by ϕ_M , ϕ_{RB} and fraction of thermal output (x) released by reburn as shown below.

Consider a reburn facility operated with total thermal rating of $\dot{P}$ [kW]. The main fuel M is fired at an equivalence ratio $\phi_M (< 1)$ such that it has a rated thermal output of $\dot{P}_M = (1 - x)\dot{P}$. The reburn fuel R is fired at $\phi_R (> 1)$ such that its rated power output is $\dot{P}_R = x\dot{P}$. The ϕ_R is adjusted so that the reburn zone equivalence ratio is ϕ_{RBZ} . Then a relation between ϕ_{RB} can be obtained in terms of ϕ_M , ϕ_{RBZ} , $\text{HHV}_{\text{O}_2, M}$ and $\text{HHV}_{\text{O}_2, RB}$ of main fuel and return fuel, and x , fraction of heat by reburn fuel:

$$\frac{1}{\phi_{RB}} = \frac{1}{\phi_{RBZ}} - \left(\frac{1-x}{x} \right) \left(\frac{\text{HHV}_{\text{O}_2, RB}}{\text{HHV}_{\text{O}_2, M}} \right) \left(\frac{1}{\phi_M} - 1 \right) \quad (3.38)$$

Since the HHV per stoichiometric O_2 flow is approximately constant, the results can be simplified as follows:

$$\frac{1}{\phi_{RB}} = \frac{1}{\phi_{RBZ}} - \left(\frac{1-x}{x} \right) \left(\frac{1}{\phi_M} - 1 \right) \quad (3.39)$$

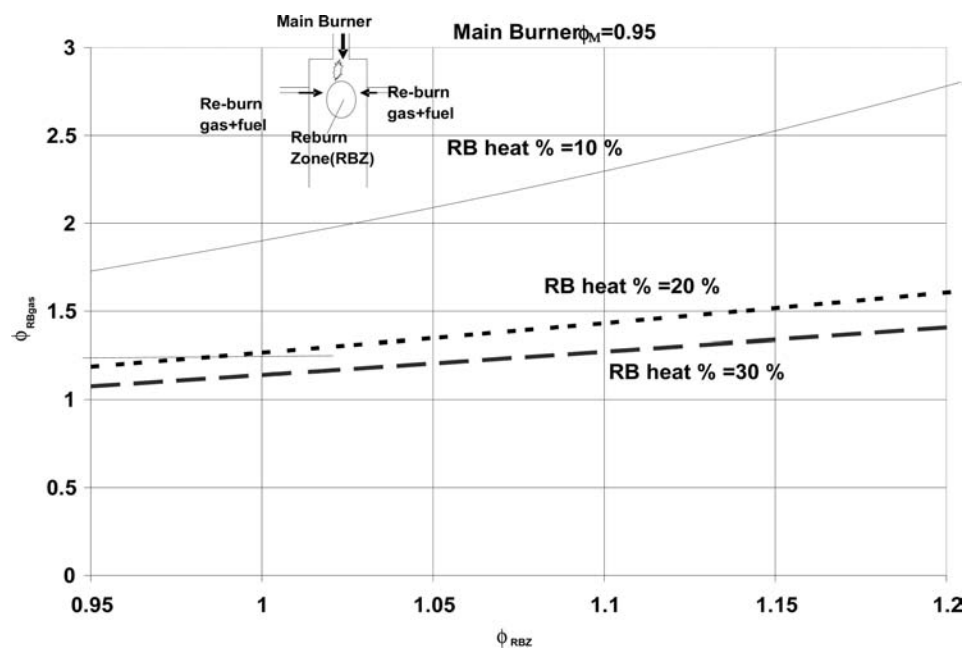


Figure 3.39. Required reburn injector equivalence ratio for desired reburn zone equivalence ratio for various reburn heat input %.

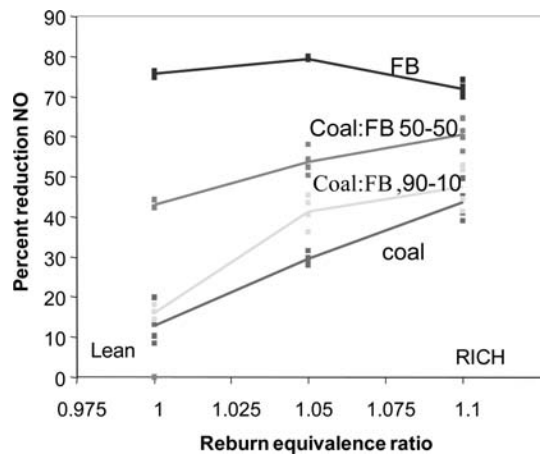
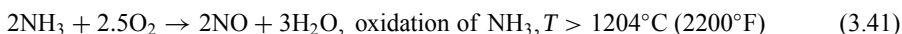
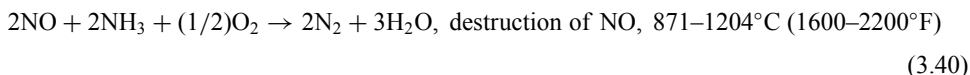


Figure 3.40. Effect of reburn zone equivalence ratio on NO_x reduction with various reburn fuels (reburn heat input = 30% of total thermal rating; main burner NO : 600 ppm) (adopted from Annamalai and Thien, 2001).

The ϕ_{RB} was adjusted to obtain the desired equivalence ratio ϕ_{RBZ} from 1 to 1.1 (Fig. 3.39). An Enerac 3000E gas analyzer is then used to measure the concentration of oxygen and NO in the final sampling port. After passing by the gas sampling port, the furnace gases are cooled by a water spray and exhausted out of the building. There is no burnout zone in the current boiler burner configuration. Figure 3.40 shows the results; it is seen that NO_x reduction is highest for FB due to (i) increased VM of FM, which reduces local O_2 , (ii) release of N probably in the form of NH_3 .

Currently, experiments are in progress on coals, and CB to determine the percentage nitrogen distribution between HCN and NH_3 . However, we have recently analyzed data presented elsewhere (Di Nola, 2009), which demonstrated that adding animal waste to coal increased the ratio of NH_3 relative to HCN. It is noted that the emissions of HCN and NH_3 are not expected under combustion conditions.

The fuel N evolved as NH_3 undergoes oxidation reaction with O_2 and reduction reactions with HCN and NH_3 . The overall competing reactions for “thermal” (i.e. temperature dependent) De- NO_x process is as follows:



The upper end of the temperature window is caused by the rapid growth of chain carriers which enhances reactions involving the oxidation of NH_2 eventually producing NO instead of reducing it (Lyon *et al.*, 1986). Sometimes the upper end could be as high as 1204°C (2200°F) (EPA). Exxon had empirically determined that NO_x reduction is effective at $T < 955^\circ\text{C}$ (1750°F). Typically reactions are faster in the presence of O_2 but not in excess amounts; these reactions suggest that the stoichiometric ratio of mole of NH_3 to mole of NO is about 1; the actual amount of NH_3 needed for the reaction is much greater than the theoretical amount because NH_3 reacts with several other gases in the flue gases, not just NO_x . The literature suggests that one needs about 0.5–3 moles of NH_3 per mole of NO_x . The Selective Noncatalytic Reduction process (SNCR) temperature window is about 900°C to 1100°C . To facilitate quick and inexpensive predictions with the thermal De- NO_x method, two competitive reaction formulations have been used for modeling purposes. One may use an empirically based model (Lyon, 1987), which includes the following forward direction only competitive reactions (Thien *et al.*, 2012):

Reaction A: $4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$ (fast)

Reaction B: $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$ (slow)

NH_3 oxidation, $> 1480\text{ K}$

$d(\text{NO})/dt$, NO production/reduction rate per unit volume, $\{\text{kmol}/(\text{m}^3 \text{ s})\} = k_B (\text{NH}_3) - k_A (\text{NH}_3)$ (NO)

$d(\text{NH}_3)/dt$, NH_3 consumption rate per unit volume, $\{\text{kmol}/(\text{m}^3 \text{ s})\} = -k_B (\text{NH}_3) - k_A (\text{NH}_3)$ (NO) where (NH_3) , (NO) concentrations in kmol/m^3 and the specific reaction rate constants k 's are defined as

$$k_A, \{\text{m}^3/(\text{kmol s})\} = 2.45 \times 10^{17} \exp\left(\frac{-29400}{T}\right), \quad T \text{ in K}$$

$$k_B, \{1/\text{s}\} = 2.21 \times 10^{14} \exp\left(\frac{-38130}{T}\right), \quad T \text{ in K}$$

Since O_2 is in excess typically and others are in trace amounts, reaction A depicts the second-order reduction of NO to N_2 and the reaction B represents the first order oxidation of NH_3 (Duo *et al.*, 1992).

It can be seen from the values of the two activation energies and the overall rate constants how the simple model was able to predict the temperature window for NO reduction (1145 to 1480 K). Figure 3.41 shows typical model results for an initial NO of 600 ppm and assumed $\text{NH}_3/\text{NO} = 2$ at 1100 K. The model results showed that when NH_3/NO was set to 1, the rate of reduction slowed down and when $\text{NH}_3/\text{NO} = 0.5$, the NO_x reduction was only 50%. While pure FB produces a

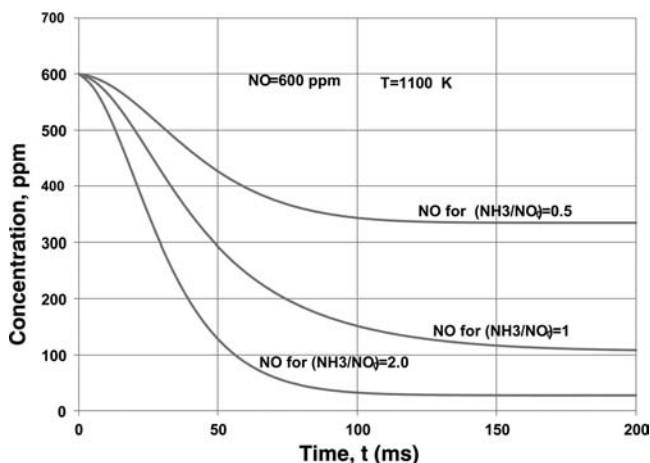


Figure 3.41. Effect of residence time on NO_x reduction by NH_3 at 1100 K.

high amount of NH_3 , coal:FB blends result in lesser NH_3 concentration; similarly lesser reburn heat input will result in lesser NO_x (Oh, 2008).

It is apparent that coal and FB can both be successfully used a reburn fuel in order to reduce NO in a boiler burner. Feedlot Biomass is almost two times more effective as a reburn fuel than coal. The NO reduction is more effective at higher reburn equivalence ratios for coal; however, the NO_x reduction is almost independent of equivalence ratio for feedlot biomass. The behavior of coal-biomass blends falls in between the behavior of coal and biomass. The greater effectiveness of feedlot biomass may be due to the release of fuel nitrogen in the form of NH_3 , and its high volatile content on a dry ash-free basis (Annamalai and Sweeten, 2005).

3.13 LOW NO_x BURNERS (LNB)

Most of the utility boilers do not use reburn with natural gas due to high cost of natural gas and development of conventional low NO_x burners where the difference between total air and primary air is split into swirling secondary air and tertiary air; i.e. air is introduced in stages to reduce O_2 availability thus reducing NO_x . A 30 kWt LNB facility has been built and tested for cofiring coal:DB blends; the reader is referred to Lawrence *et al.* (2012) and Lawrence (2013) for more details on facility, experiments and results from cofiring in LNB. However this LNB facility used overfire air as tertiary air. Dairy biomass is evaluated as a cofiring fuel with Wyoming Powder River Basin subbituminous coal in a small scale 30 kWt burner boiler facility equipped with air staged combustion for low NO_x control. The cofiring experiments were performed with 90:10 (by mass percent) coal: dairy biomass blended fuels as well as pure coal. Standard emissions from solid fuel combustion (O_2 , CO_2 , CO, NO_x , and SO_2) were measured in addition to the temperature profile along the axial length of the furnace. In addition to these emissions measurements, NO_x on a heat basis (g/GJ) was calculated. Figure 3.42 shows the preliminary results on variation in NO_x emission with % tertiary air; when compared to PRB, only about 12% reduction in NO_x was obtained.

3.14 GASIFICATION

In previous experiments the effects of blending coal with relatively high-ash/low energy content cattle feedlot biomass (FB) at 50:50 ratio, and by blending coal with LB also at 50:50 ratios were

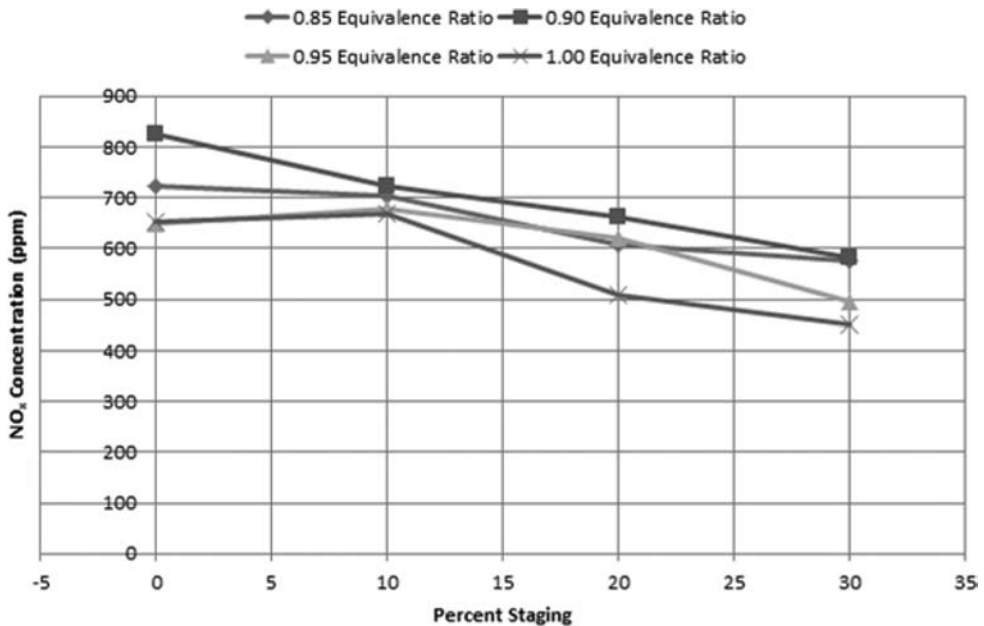


Figure 3.42. NO_x emissions for staged 90-10 PRB-LADB. The equivalence ratio is overall equivalence ratio of the facility. It is proven conclusively that staging can reduce NO_x. (Adopted from Lawrence, 2013)

determined in a fixed-bed gasification configuration (Priyadarshan *et al.*, 2005). Experiments were performed on gasification of coal and CB.

There have been a few studies on non-biological gasification of high moisture/high ash manure biomass. For example, an advanced gasification system discussed by (Young *et al.*, 2003) used separated DB solids pressed to 70% moisture from an auger press in a high temperature, air blown gasifier to produce synthetic gas. The gas was then fired in an IC engine to generate electrical power. The dairy was able to produce twice its electrical energy requirement from the synthetic gas. A detailed review of the literature is presented in Gordillo (2009) and Thanapal (2010). Researchers at Texas A&M University used a 10 kW adiabatic fixed bed counter current gasifier to study the gasification of dairy biomass using air, air-steam, enriched air and CO₂:O₂ mixtures as gasification mediums.

3.14.1 Experimental setup

The current experiments were performed using a modified small-scale (10 kW) batch type fixed bed counter flow gasifier (FBCFG, Fig. 3.43). The gasifier (72 cm tall) is divided into 4 sections, which are joined by using ring type flanges of ½ in × 14 in × 20 in. The gasifier is constructed of castable alumina refractory tube (inner and outer diameter of 13.9 cm (6 in) and 24.5 cm (10 in), respectively) which is surrounded by 4.45 cm (1¾ in) of insulating blanket in order to minimize heat losses. The layer is then surrounded by a steel outer tube with an inner diameter of 34.3 cm (13½ in). An ash disposal system was installed to maintain quasi-steady operation. A conical gyratory cast iron grate drilled with a large number of ¼ in holes was coupled to a pneumatic vibrator of variable frequency that maintains the grate in continuous vibration in order to dispose the ash continuously from the bed. The rate of ash removed can be controlled by changing the vibrational frequency in the vibrator. The ash from the plenum was periodically removed. The fuel is supplied at the top of the gasifier while the mixture of air and steam is supplied at the bottom

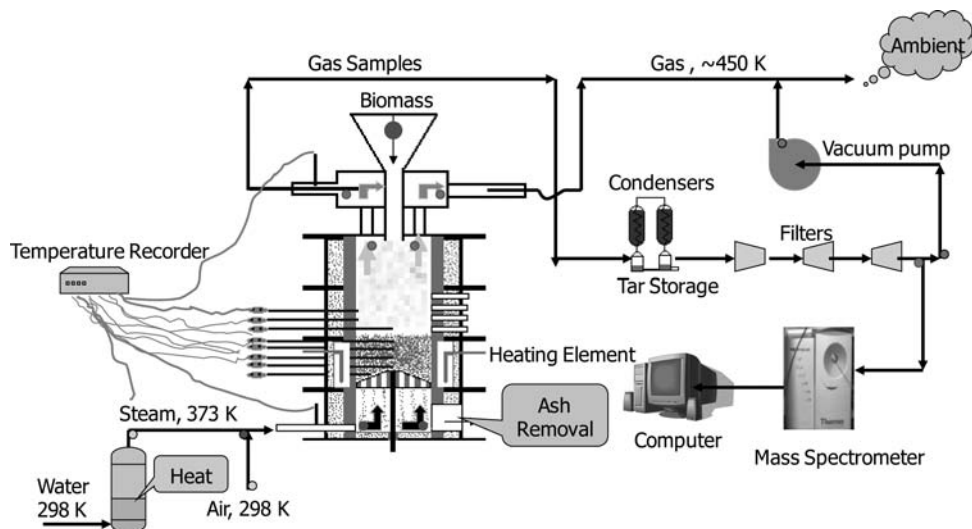


Figure 3.43. Schematic gasification facility (adopted from Gordillo, 2009).

(plenum). The steam is generated by a steam generator built with a cylindrical 4-inch internal diameter vessel heated by a (1.2 kW) type tape heating element rolled around of the vessel with variable power output (0.1 to 1.2 kW); thus, the steam production rate can be controlled from 0.1 to 1.5 kg/h by changing the power supplied to the heater element. The sampling unit is composed of two condensers cooled with ice-cold water (0°C) to condense out the tar and the H_2O in the products and a filter system to retain the particulate material. The temperature of the bed is measured every 60 seconds using K-type thermocouples (Cr-Al) placed at 8 locations along the gasifier axis. The gas samples are analyzed by a mass spectrometer (MS) continuously at real time (Gordillo, 2009).

3.14.2 Experimentation

The gasification experiments were performed for the following cases:

(a) Base case

- Bed height at 17 cm ($\sim 6\frac{3}{4}$ ")
- Fuel: low ash separated solids dairy biomass (LA-PC-sepsol-DB).
- Particulate size, $d_p = \sim 6.25$ cm ($1/4$ ") for DB and ~ 3 mm ($\sim 1/8$ ") for coal
- Fuel flow rate 1 kg/h (2.2046 lbm/h)
- Air flow ~ 1.13 normal m^3/h (40 SCFH) at 298 K (536 R)
- Steam flow rate at 0.3 kg/h (~ 0.66 lb/h)
- Equivalence ratio (ER) at 3.18
- Steam to fuel ratio ($S:F$) at 0.68

(b) Parametric cases

- Fuel: LA-PC-Sepsol-DB, Coal-LA-PC-Sepsol-DB blend (90% LA-PC-Spsol-DB, 10% coal), and Ash - LA-PC-Sepsol-DB blend (90% LA-PC-Sepsol-DB, 10% ash)
- Air flow between 0.57 and 2.26 normal m^3/h (20 and 80 SCFH) at 298 K (536.4 R)
- Steam flow rate between 0.18 and 0.5 kg/h (0.4 and 1.1 lb/h) at 373 K (671.4 R)
- Equivalence ratio (ER) between 1.59 and 6.36
- Steam to fuel ratio ($S:F$) between 0.35 and 0.8

- Experiments with (i) DB-coal blends (90% DB-10% Coal) (ii) DB-ash blends (90% DB-10% ash) were used in order to determine catalytic effect if any on gasification.

3.14.3 Experimental procedure

A normal experiment started with preheating the grate and the combustion chamber using a propane torch placed under the grate. When the temperature in the combustion chamber (2 cm above the grate) reached 800°C (after ~2 hours), the torch was turned off and biomass was added to the gasifier. The addition continued until the bed height attained 17 cm; afterwards, the fuel port was closed and the flows of steam and air were adjusted to the desired experimental conditions. As the biomass was pyrolyzed and the char was burned the bed height started decreasing and the ash accumulated. Thus, biomass was added every 10 minutes and in batches as required. In the earlier batch experiments reported by Priyadarsan *et al.* (2004), there was no ash disposal system; as such the temperature peak moved towards the bed surface due to ash accumulation at the bottom. In the current experiments, the ash was disposed of continuously and a quasi-steady state was assured by maintaining the peak temperature at the same location in the ash disposal system. When the peak temperature achieved a steady state (~1.0 hours) the gas sampling unit was turned on and the gas analysis was performed continuously during 20 minutes by the mass spectrometer (MS).

The flow rate of dairy biomass was maintained constant at 1 kg/h and the flows of air (0.56–2.26 SATP m³/h (standard ambient temperature and pressure meter cube per hour)) at 15°C and steam (0.19–0.43 kg/h) at 100°C were changed in order to obtain the desired experimental conditions: $ER = 1.59, 2.12, 3.18, 4.24, \text{ and } 6.36$ and $S:F = 0.35, 0.56, 0.68, \text{ and } 0.80$. An air drier was used to dry the air before it was supplied to the gasifier. The gasifier was operated at 98 Pa vacuum pressure during all the experimentation. Temperatures along the gasifier were monitored at every 60 seconds by type K thermocouples located at 0.02, 0.04, 0.07, 0.13, 0.20, 0.24, and 0.28 m above of the grate. Samples were taken at the top of the gasifier at the rate of 0.14 SATP m³/h and conditioned by the sampling unit in order to remove tar and particulate material. The mole fractions of CO₂, CO, CH₄, C₂H₆, O₂, H₂, and N₂ were measured every ten seconds by the MS. The same procedure used for the air gasification was again employed for enriched air gasification with little changes.

3.14.4 Results and discussion

3.14.4.1 Fuel properties

Ultimate and proximate analysis (on an as received basis) of the DB (separated solids) used as feedstock in the current gasification experiments are presented in Table 3.3. Using as received analysis (ar), dry and dry ash-free (DAF) values are calculated and reported. Also, empirical chemical formulae are presented in Table 3.3 for gasification of DAF DB. Air gasification of DAF DB at $ER > 5.8$ (or $A:F < 0.87$) implies insufficient oxygen for the reaction ($C + \frac{1}{2}O_2 \rightarrow CO$) and hence, incomplete conversion of char, which means char as byproduct. On the other hand, at $ER < 5.8$ (or $A:F > 0.87$) there is more oxygen than that required for the conversion of all FC to CO and the FC could be gasified completely to CO and CO₂. However, in gasification processes where the reaction time is not infinity (not ideal), incomplete conversion of char can be possible even with $ER < 5.8$.

3.14.4.2 Experimental results and discussion

To estimate the uncertainty in gas composition, standard deviation was determined for the data. The uncertainty for each gas was calculated as the ratio between the standard deviation and the average value measured. Additionally, the uncertainty of the temperatures was estimated as the ratio between the uncertainty of the device ($\pm 1.5^\circ\text{C}$) and the measured value. In general, the gas composition values fluctuated within ~15% and the temperature values within ~0.55% of the average value measured.

3.14.4.2.1 Temperature profiles for air gasification

Temperature profiles are measured every 60 seconds along the gasifier axis. A typical gas analysis is presented in Figure 3.44a for an experiment at $ER = 3.18$ and $S:F = 0.8$. It is apparent that the temperature profile achieves almost state steady in the last ten minutes; therefore, it is appropriate to assume steady state conditions during the last 10 minutes of each gas analysis. The temperature profiles discussed in this paper correspond to the average measured during the last ten minutes. As discussed before, in a fixed bed gasifier, the oxidation of char (heterogeneous oxidations) occurs near to the bottom of the bed where mostly char reacts with the oxygen and steam to produce CO , CO_2 , H_2 , and the heat required for driving the gasification process is released. Because under gasification conditions char oxidation of large particles is almost diffusion controlled, the char oxidation rate is dependent upon the availability of O_2 in the gas stream. The temperature in the combustion zone (T_{peak}) depends upon the concentrations of O_2 , H_2O , and CO_2 . Above the combustion zone, the temperature decreases since oxygen concentration is negligible and most of the reactions occurring there are endothermic. Below the combustion zone, the temperature is lower because it corresponds to ash temperature. It is apparent from Figure 3.44a that the peak temperature occurred at ~ 5 cm above of the grate indicating no ash accumulation.

Increase of ER , at fixed $S:F$ ratio implies a decrease in the oxygen supplied; thus, heat generation due to char oxidation decreases resulting in lower T_{peak} and hence results in a lower temperature

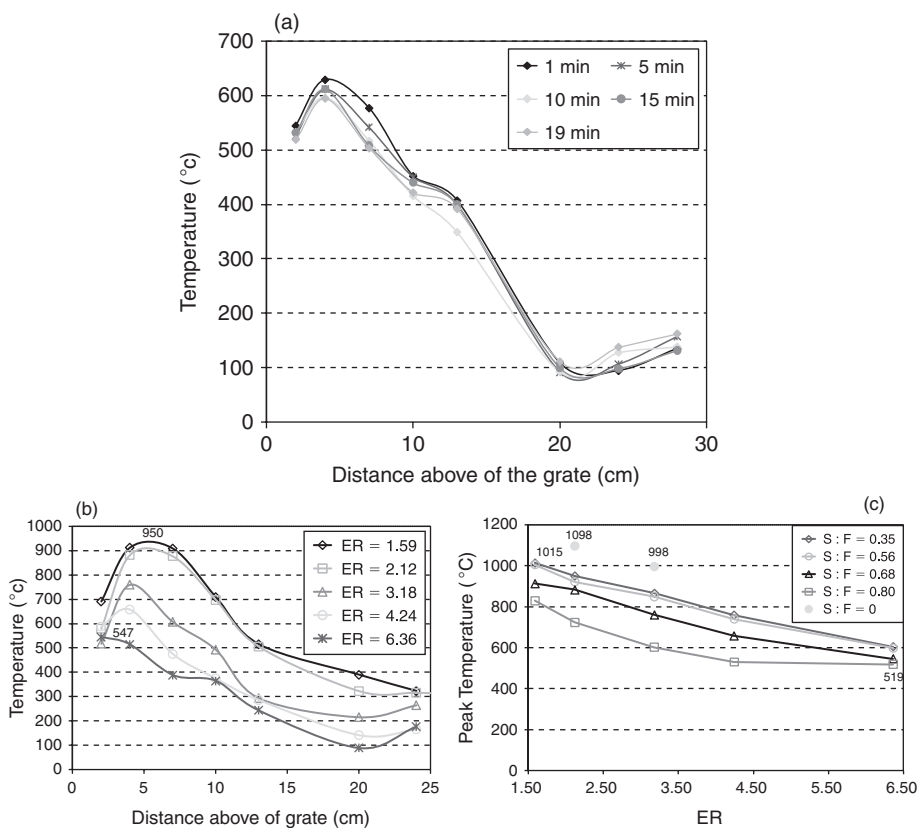


Figure 3.44. (a) Temperature profile during a typical gas analysis at $ER = 3.18$ and $S:F = 0.8$, (b) temperature profile along the gasifier axis for several ER s and $S:F = 0.68$, (c) peak temperature profile vs. ER for several $S:F$ ratios (adopted from Gordillo, 2009).

profile (Fig. 3.44b). Due to the presence of oxygen at the bottom of the bed, the peak temperature occurs near the bottom. The temperature of the particle under the assumption of negligible char-steam reaction and diffusion-controlled combustion can be derived as (Annamalai and Puri, 2007):

$$\frac{c_p(T_p - T_\infty)}{h_c} = B \quad (3.42)$$

where $h_c = h_{c,I}$ for CO, $h_c = h_{c,II}$ for CO₂ produced, T_p = particle temperature, $B = \{Y_{O_2\infty}/\nu_{O_2}\}$, $\nu_{O_2} = 1.33$ for CO, 2.33 for CO₂ produced, $Y_{O_2\infty}$ = Oxygen mass fraction, and c_p specific heat of the gases. In particular, for $ER = 1.59$ and S:F = 0.68 the peak temperature measured is about 950°C (Fig. 3.44b); however, this value is lower compared to (1191°C) obtained with the equation 3.42 (c_p of air = 1.15 kJ/kg K, c_p of the steam = 2.3 kJ/kg K, c_p of mixture = 1.28 kJ/kg K, $Y_{O_2\infty} = 0.203$, and $h_{c,I} = 9204$ kJ/kg). The lower experimental temperature compared to that of the model indicates that (i) the char may react with both O₂ and steam at the bottom of the bed to produce CO and H₂ and (ii) combustion may not be diffusion controlled. On the other hand, if the steam carbon reaction was included in the model and if diffusion limited heterogeneous reactions was assumed, the estimated T_p would be lower than the estimated using equation 3.42.

Figure 3.44c shows the effect of change in ER s and S:F ratio on the peak temperature (combustion temperature zone). Also are presented two T_{peak} (1098 and 998°C) obtained for gasification with only air at $ER = 2.12$ and $ER = 3.18$. At lower ER s, the effect of the S:F ratio is higher. For instance, at $ER = 1.59$ the peak temperature difference between the curves of S:F = 0.35 and 0.80 is 185°C while at $ER = 6.36$ the difference between the same curves is 91°C only since oxygen availability is limited. The curves from Figure 3.44c suggest that at constant S:F, the peak temperature is affected almost linearly by changes on the ER . Increased S:F causes the T_{peak} to decrease. This can occur due to (i) decreased amount of air, (ii) change in the c_p of the mixture, (iii) regimes of combustion: kinetics vs. diffusion controlled, and (iv) steam-char reaction. At $ER = 2.12$, the peak temperature for gasification with air only is 147°C (15.45%) higher as compared to that of gasification with air-steam at $ER = 2.12$ and S:F = 0.35 while at $ER = 3.18$, the difference in peak temperature between gasification with air and gasification with air-steam is ~132°C (15.24%). In general, for the range of operating conditions (ER and S:F) investigated the T_{peak} ranged between 519 ($ER = 6.36$, almost pure pyrolysis) and 1015°C ($ER = 1.59$).

3.14.4.2.2 Temperature profiles for enriched air gasification and CO₂:O₂ gasification

For the gasification experiments with higher oxygen percentages, at $ER = 2.1$ and S:F = 0, the temperature profiles obtained are plotted in Figure 3.45. The peak temperatures obtained can be compared to that of the theoretical values obtained using the B number.

From Figure 3.45, the peak temperature obtained when using enriched air mixtures is observed to increase with increased oxygen concentration. The numbers obtained experimentally were almost same as the values calculated theoretically using B number calculations.

Enriched air results in the presence of nitrogen in syngas, which lowers the heat value of gases. Also, carbon dioxide (CO₂) can be separated easily from products compared to nitrogen (N₂) in the event CO₂ sequestration is necessary to enhance the heat values. Hence, experiments were performed using carbon dioxide-oxygen mixture as the gasification medium instead of air. In this case, carbon dioxide is substituted for nitrogen in the air mixture. Also the carbon dioxide produced as a result of gasification can be separated and circulated again into the reactor at high temperatures (e.g. as cooling medium for the gasifier) in order to increase the efficiency of the reactor and also to sustain the reaction within the gasifier. This will also increase the upper limit on ER . This in turn helps to reduce the amount of carbon dioxide released into the environment. CO₂ has a slightly higher specific heat (c_p) than N₂ at higher temperatures. The c_p of the mixture of CO₂ and O₂ is higher than c_p of the mixture of N₂ and O₂. Hence, T_{peak} , using CO₂ instead of N₂, is expected to be low. The difference in peak temperatures can be observed in the temperature profiles (Fig. 3.46) obtained using carbon dioxide in the gasifying medium instead of nitrogen (Thanapal *et al.*, 2012).

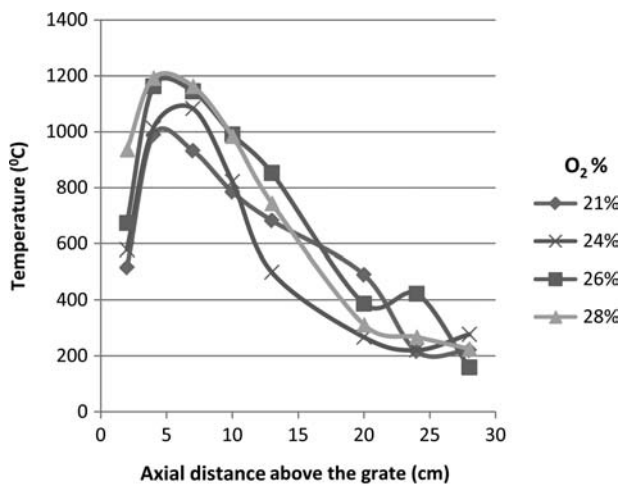


Figure 3.45. Steady state temperature profile, $ER = 2.1$, $S:F = 0$ (adopted from Thanapal, 2010).

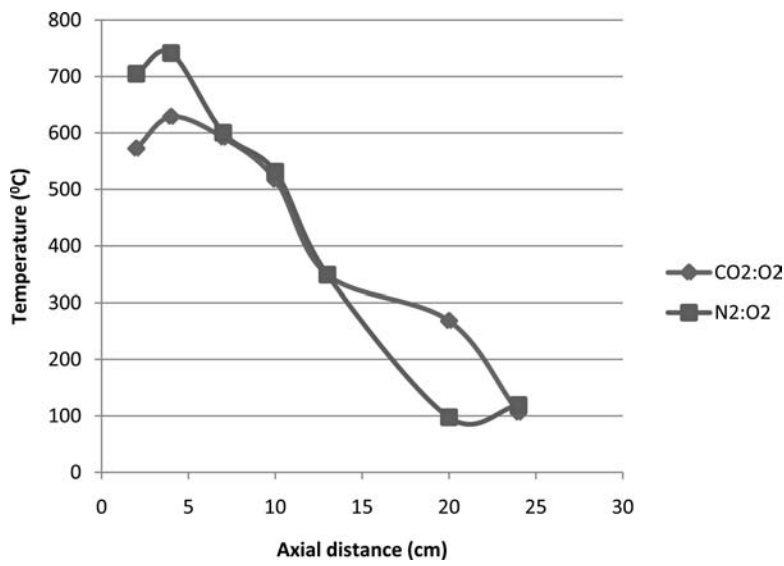


Figure 3.46. Temperature profile, 21% oxygen, $ER = 4.2$, $S:F = 0$ (adopted from Thanapal, 2010).

3.14.4.2.3 Gas composition results with air

The results on gas analysis obtained from MS for a typical experiment ($ER = 4.24$ and $S:F = 0.35$) are shown in Figure 3.47a as a function of the time. The data on gas composition have a cyclic dynamic behavior in the vicinity of an average value. However, at first glimpse, it appears that the average is almost constant during the experimental period. Figure 3.47a shows the mole fraction of N_2 , H_2 , CO_2 , CO , CH_4 , and C_2H_6 (on a dry basis) along with the average mole fraction and the standard deviation (STDEV) of the data. The data on H_2 present the major standard deviation (3.2) about of the average value of 18.62% whereas the data on CH_4 , CO_2 , and C_2H_6 show a lower standard deviation and the data on CO shows a standard deviation of 1.53. As discussed

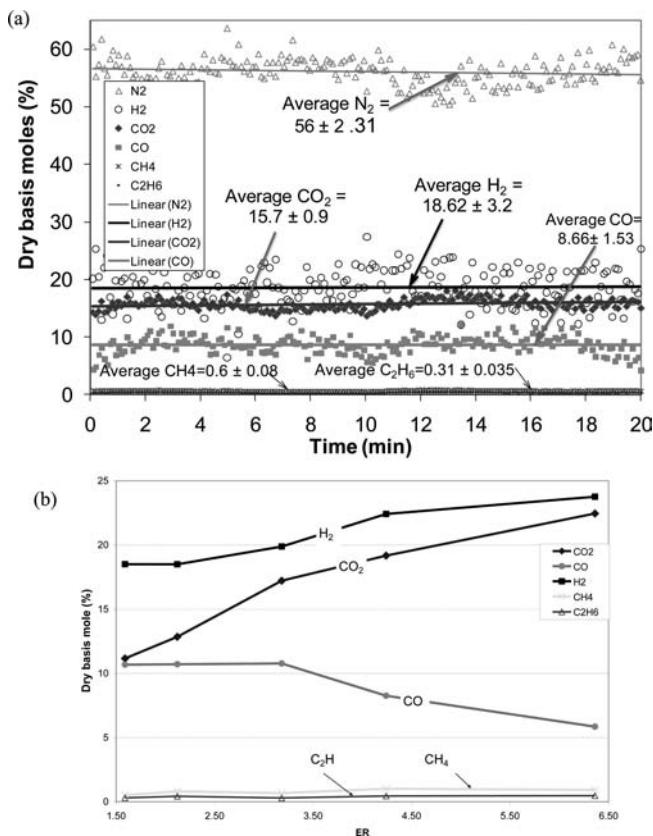


Figure 3.47. (a) Gas composition vs. time for a typical experiment at $ER = 4.24$ and $S:F = 0.35$, (b) gas composition for several ER s and $S:F = 0.68$ (adopted from Gordillo, 2009).

earlier, in general for the set of experiments discussed in this paper, the composition value of the gases analyzed fluctuated within $\pm 15\%$ of the average value.

As discussed before, at constant $S:F$, increasing the ER decreases the O_2 supplied with the air at the bottom that implies decreasing T_{peak} in the combustion zone. Then, as the temperature is lowered, the reaction $C + O_2 \rightarrow CO_2$ is favored. CO_2 increases at lower temperatures. More production of CO_2 implies consumption of more O_2 via CO_2 , thus, less O_2 is consumed via CO and hence less CO is produced (Fig. 3.47b). Also, at constant $S:F$, increased ER increases the steam-air ratio ($S:A$), which implies decreased air supplied and hence the combustion of char takes place in a H_2O -rich mixture which favors the heterogeneous reaction of char with H_2O to produce H_2 . The rate of H_2 and CO produced by the heterogeneous reaction $C + H_2O \rightarrow CO + H_2$ becomes important when the reaction occurs at low O_2 . On the other hand, the concentrations of CH_4 and C_2H_6 were lower ($0.43 < CH_4 < 1.75$ and $0.2 < C_2H_6 < 0.7$) as compared with those of other gases and were almost not affected by the ER .

The effect of the ER and $S:F$ ratio on the concentrations of H_2 , CO , and CO_2 are presented in Figure 3.48a, Figure 3.48b, and Figure 3.48c. At constant ER , higher $S:F$ ratios signify more steam available to react with char to produce CO and H_2 (steam char reaction) in the high temperature reducing zone immediately above the combustion zone (i.e. O_2 deficient) near the bottom of the bed. The CO produced by the steam reforming reaction reacts with the surplus steam (shift reaction) in the upper zone (reduction) to produce more H_2 and CO_2 ; hence, more C atoms contained in the DB result in CO_2 . It is evident from the graphs of Figure 3.48b that lower ER s

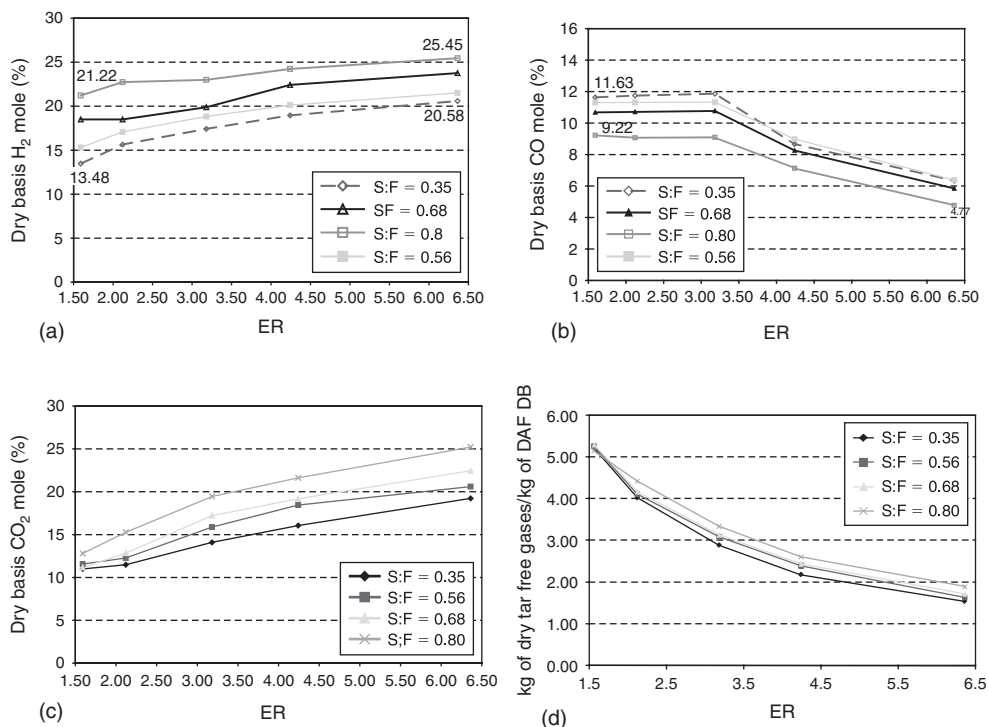


Figure 3.48. (a) Hydrogen% vs. ER for several S:F ratios, (b) carbon monoxide% vs. ER for several S:F ratios, (c) carbon dioxide% vs. ER for several S:F ratios, (d) mass of gases produced per kg of DAF DB on a dry tar free basis for gasification of pure DB (adopted from Gordillo, 2009).

have a lower effect on the CO production compared to higher ER s. Also, the results show that at constant ER , changing the S:F ratio affects the production of H₂ more than the production of CO. For instance, at $ER = 1.59$ changing the S:F from 0.35 to 0.8 increases the production of H₂ by 57.5% but decreases the production of CO by only 26.2% (Figs. 3.48a,b). Since the decrease in CO% is less than the increase in H₂% then there must be a heterogeneous steam char reaction resulting in production of H₂. This is also evident from the lowered T_{peak} . Under the operating conditions discussed ($1.59 < ER < 6.36$ and $0.35 < S:F < 0.80$), the CO ranged from ~ 4.77 to $\sim 11.73\%$, H₂ from 13.48 to 25.45%, CO₂ from 11 to 25.2%, CH₄ from 0.43 to 1.73%, and C₂H₆ from 0.2 to 0.69%.

3.14.4.2.4 Gas composition results with enriched air and CO₂:O₂ mixture

Figure 3.49 shows the gas composition obtained for enriched air gasification with $ER = 2.1$. The percentage of carbon dioxide produced increased with increased oxygen percentage due to higher oxygen concentration in the incoming gasification medium. It was accompanied by a decrease in carbon monoxide and an increased production of hydrogen.

Figure 3.50 shows the comparison between the gas composition at 21% O₂ obtained for the gasification with air and carbon dioxide at $ER = 4.2$.

Since carbon dioxide replaced nitrogen in the air the gases produced during gasification had a higher percentage of carbon dioxide, which possibly includes carbon dioxide produced during gasification as well as the carbon dioxide coming in as the gasifying medium. In addition, the heating value of the gases produced using carbon dioxide as the gasifying medium was higher when compared to that of air gasification having nitrogen.

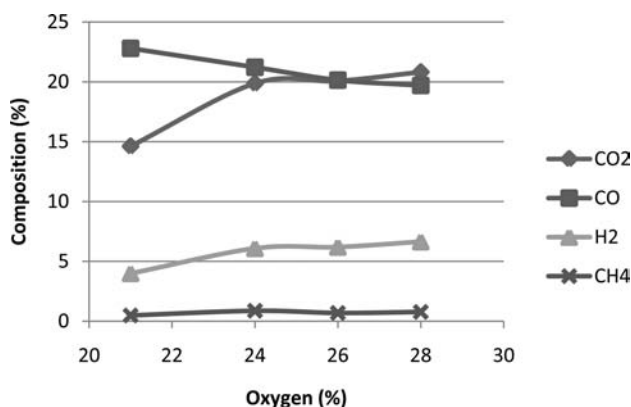


Figure 3.49. Gas composition for enriched air gasification, $ER = 2.1$, $S:F = 0$ (adopted from Thanapal, 2010).

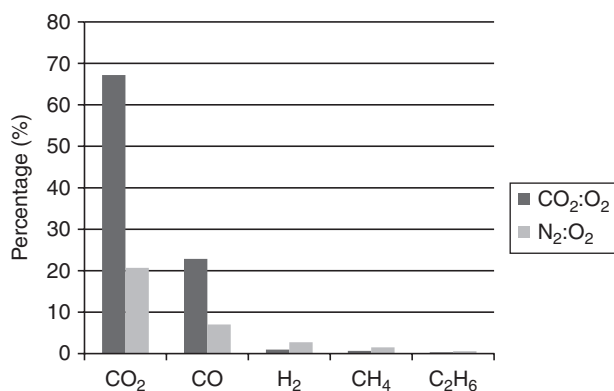


Figure 3.50. Gas composition, 21% oxygen, $ER = 4.2$, $S:F = 0$ (adopted from Thanapal, 2010).

3.14.4.2.5 HHV of gases and energy conversion efficiency

The heat content of the combustible gases is computed on a dry tar-free basis. The energy density [kJ/m^3] of the gases is represented in Table 3.10 for several ER and $S:F$ ratios. Increased ER or $S:F$ tends to increase the energy density of the gases; this is due principally to the increase in the production of hydrocarbons (HC) and H_2 . At constant $S:F$, increasing the ER tends to increase the HHV , due to more H_2 and HC, until a certain ER beyond which the HHV starts to decrease. The energy density of the gases is strongly affected by the production of hydrocarbons such as CH_4 and C_2H_6 , which have a high HHV as compared to the other gases (CO and H_2). For example, the HHV or energy density of the CH_4 is $36264 \text{ kJ/SATP m}^3$ while the HHV of CO and H_2 are 11550 and $11700 \text{ kJ/SATP m}^3$ respectively. Although the HHV of the H_2 (141800 kJ/kg) on a mass basis is very high, its energy density is almost comparable to that of CO (only 1.08% higher) due to its low density ($\sim 0.0857 \text{ kg/m}^3$). At constant ER , increased $S:F$ increase the H_2/CO of the species produced (Fig. 3.49 and Fig. 3.50), which implies increasing the energy density slightly. For the set of operating conditions investigated the HHV of the gases ranged between 3268 and 4285 kJ/SATP m^3 , which correspond to a range between 9 and 12.6% of the energy density of the CH_4 on a volume basis. Even though the energy density of the gases gives an idea of the energy content of the gases produced, it does not give information about the degree of energy conversion from biomass gasified.

Table 3.10. Energy density of the gases (kJ/Standard temperature and pressure (SATP) m³) for several *ER*s and *S:F*s, adopted from Gordillo (2009).

<i>S:F</i> (mole ratio)	<i>ER</i>				
	1.56	2.12	3.18	4.24	6.36
0.35	3280	3473	3787	3648	3666
0.56	3268	3835	4402	4245	4032
0.68	3762	3955	3993	4217	4079
0.80	3934	4116	4291	4378	4585

Table 3.11. Heating value of the syngas obtained using enriched air, adopted from Thanapal *et al.* (2012).

	21% <i>ER</i> = 2.1 <i>S:F</i> = 0	21% <i>ER</i> = 2.8 <i>S:F</i> = 0	21% <i>ER</i> = 4.2 <i>S:F</i> = 0	21% <i>ER</i> = 2.8 <i>S:F</i> = 0.33	21% <i>ER</i> = 4.2 <i>S:F</i> = 0.33	28% <i>ER</i> = 2.1 <i>S:F</i> = 0	28% <i>ER</i> = 2.8 <i>S:F</i> = 0	28% <i>ER</i> = 4.2 <i>S:F</i> = 0	28% <i>ER</i> = 2.8 <i>S:F</i> = 0.33	28% <i>ER</i> = 4.2 <i>S:F</i> = 0.33
<i>HHV</i> [kJ/kg]	3245	2699	1709	2766	2070	3648	2720	2205	4333	3002
<i>HHV</i> [kJ/Nm ³]	4167	3470	2219	3401	2598	4670	3711	2922	5351	3860
<i>HHV</i> with N ₂ & CO ₂ [% CH ₄]	10.52	8.76	5.60	8.58	6.56	11.79	9.37	7.38	13.51	9.74
<i>HHV</i> without N ₂ & CO ₂ [% CH ₄]	37.01	40.47	47.29	42.36	43.07	40.41	40.19	42.69	39	41.11

Variation of *HHV* with *ER* in the presence and absence of steam for the case of air (21% O₂) and enriched air mixtures (28% O₂) is shown in Table 3.11. The enriched-air medium results in gas with higher *HHV*. The amount of hydrogen produced increases in the presence of steam, but the *HHV* based on mass is less even with H₂ due to lower molecular weight of H₂. For both air gasification and enriched-air gasification, we observe a decrease in *HHV* with *ER*. Table 3.11 also gives the *HHV* of the gas mixture with inerts (N₂ and CO₂) and without inerts (N₂ and CO₂) and these values are expressed in terms of percentage *HHV* of natural gas (Thanapal *et al.*, 2012).

Ultimate analyses of samples of tar collected in the sample unit were obtained and were used to derive an empirical formula (CH₂O_{0.48}N_{0.064}S_{0.0017}). Because it was impossible to measure the mass of tar and H₂O produced during the experiments, the volumetric flow of gases, required to calculate the energy recovery was estimated by mass balance using tar and gas compositions and with the knowledge of the char produced and the flows of the air and steam. Table 3.12 presents the energy conversion efficiency (*ECE*) estimated by atom balance and assuming gas composition on a dry tar free basis. Although, the energy density of the gases tends to increase with increased *ER*s, the *ECE* decreases, because increased *ER*s produce more mass of tar and char but less mass of gases per kg of DB gasified.

For the range of the operating conditions studied, the *ECE* ranged from 0.24 to 0.69; the remaining fraction corresponds to the energy in char, tar, and sensible heat of gases leaving the gasifier. This agrees with the fact that in a fixed bed gasifier the gases leave the gasifier at a lower temperature as compared to that of gases leaving a fluidized bed gasifier. Lower sensible heat of gases leaving the reactor implies higher gasifier efficiency, and hence more energy recovered in the gases.

Table 3.12. Energy conversion efficiency (*ECE*) for several *ER*s and *S:F*s estimated by atom balance, adopted from Gordillo (2009).

<i>S:F</i> (mole ratio)	<i>ER</i>				
	1.56	2.12	3.18	4.24	6.36
0.35	0.65	0.56	0.45	0.33	0.24
0.56	0.60	0.59	0.53	0.41	0.27
0.68	0.69	0.60	0.47	0.41	0.29
0.80	0.69	0.64	0.53	0.44	0.35

3.15 SUMMARY AND CONCLUSIONS

The utilization of animal manure in combustion facilities can help ease the impacts large CAFOs, including dairies, have on the environment. DB had a lower heat content due to less fixed carbon, more oxygen, and more ash; furthermore, it contained more fuel-bound nitrogen:

- DB can be successfully blended with coal and cofired in a furnace.
- High ash content of HA-PC-DB-SoilS made it a poor quality fuel.
- Large power plant facilities can benefit from animal biomass due to displacement of current fossil fuels such as coal and emissions reduction.
- Co-firing has minimal effect on burnt fraction (*BF*). *BF* was independent of fuel type. *BF* was almost unity when operating near stoichiometric.
- Co-firing increased NO_x in lean combustion, however; NO_x was reduced by blending coal with DB in rich combustion.
- When co-firing with coal under rich conditions, cattle biomass (CB) has the potential to reduce NO_x and Hg emissions.
- Gasifying CB with air and air-steam oxidizing agents can produce synthetic gases which can be used in different combustion systems.
- Carbon dioxide-oxygen gasification in the presence of carbon dioxide instead of nitrogen can be used to get lower peak temperatures even with increased oxygen concentration within the reactor owing to the higher specific heat of carbon dioxide when compared to that of nitrogen. In addition, the carbon dioxide produced during gasification can be separated and re-circulated thereby reducing the emission of carbon dioxide into the environment.

The relative cost of coal and the distance between the combustion facility and the CAFO greatly influence the economic viability of a biomass combustion retrofit project.

ACKNOWLEDGEMENT

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CHAPTER 4

Co-combustion coal and bioenergy and biomass gasification: Chinese experiences

Changqing Dong & Xiaoying Hu

4.1 BIOMASS RESOURCES IN CHINA

In order to reduce the use of fossil fuel and the negative effects on climate, China has issued a Renewable Energy Law, which came into effect on 1st January 2006, to promote the development and utilization of renewable energy in China. In 2010, 76.8% of electricity generated in China was from coal (containing coal gangue): this corresponds to 3249 TWh, nearly 1100 million tonnes of coal burned and over 1800 million tonnes of CO₂.

Along with the growing of social demand on energy, as the main energy source fossil fuels are decreasing rapidly. Therefore, looking for a renewable energy is being paid more and more attention by society, which becomes a focal point. Biomass is a source of renewable energy, which is considered one of the best forms of alternative energy. Biomass energy comes in many forms and the major sources of biomass are agriculture, food-processing residues, industrial wastes, municipal sewage and household garbage. Biomass accounts for 35% of primary energy consumption in developing countries, raising the world total to 14% of primary energy consumption. Biomass – the fourth largest energy source after coal, oil and natural gas – is the largest and most important renewable energy option at present and can be used to produce different forms of energy. It is reported that the annual yield of natural cellulosic biomass in China exceeds 0.7 billion tonnes, in which the amount of corn stalks are around 220 million tonnes. It was assumed about 50% of the agriculture waste can be used as energy, for power generation, heat supply and cooking. It is scheduled that biomass power generation capacity in China will reach 3000 MW in 2020.

4.1.1 *Agricultural residues*

Agricultural residues mainly refer to straw, stalks and husk of crops. In China, the main crops include rice, wheat, corn, beans, tubers, sorghum, coarse grains, oil bearing crops, cotton and sugarcane (Li *et al.*, 2005). Presently, the usage of agricultural residues include cooking and heating in rural households, fertilizer, forage and the raw material of paper (Li *et al.*, 2005). The forest residues are usually categorized into this type especially in agricultural areas. They come from fuel wood and waste of forest industries which are widely available in rural China but with unbalanced distribution (Li *et al.*, 2001).

Agricultural residues can be identified as two types. Primary residues are the biomass generated during the harvest (e.g. rice straw, sugar cane tops) which are usually used as fertilizer or animal feed and are hard to collect (Bhattacharya *et al.*, 2005). Comparably, secondary residues refer to the co-produced residues during the further processing after harvest such as rice husk and bagasse. Relatively large quantities of secondary residues are easy to get at the processing site without further transportation and handling cost (Li *et al.*, 2005) and thereby are considered as a suitable biomass resource for commercial purpose of energy generation. Energy potential from agriculture is expected to be 5.31 EJ in 2010 (Bhattacharya *et al.*, 2005). However, few

Table 4.1. The regional distribution of agricultural residues in China.

Region	Total	Per capita	Typical provinces
North China	6540.1	0.79	Shanxi, Hebei
Northeast China	7638.0	1.63	Jilin, Liaoning
Middle-south China	12324.8	0.50	Hubei, Hunan
East China	12998.7	0.56	Shandong, Jiangsu
Southwest China	6289.7	0.48	Sichuan, Yunnan
Northwest China	3974.5	0.75	Gansu, Qinghai

Source: National Development and Reform Commission (NDRC), 2008.

data are available about distribution between primary and secondary residues and further work is required here.

In general, agricultural residues are widely available in China but with unbalanced distribution among regions (Li *et al.*, 2001). East and middle-south China have the largest portion of total production (in order of 10,000 tonnes/y) while Northeast China has the highest per capita production (in order of 100 kg/y), which is shown in Table 4.1. For energy purposes, a three-stage calculation model has been developed by the National Development and Reform Commission (NDRC, 2008), the total production, the accessible amount and the energy potential. According to NDCR's data for 2005, 0.3 billion tonnes of agricultural residues can be used for energy purposes which is equal to 0.15 billion tonnes standard coal.

4.1.2 Livestock manure

Livestock manure refers to animal dung and waste which has been used for centuries as a fertilizer for farming. According to the Renewable Energy Development Project (REDP, 2005), nearly 80 billion cubic meters of biogas, which equals 57 million tonnes of standard coal equivalent are generated from farming and the agriculture industry in China (Li *et al.*, 2001).

With the great change of food choice on Chinese people's tables, livestock production has been expanded to meet increasing demand for meat, egg and dairy products. Due to N_2O and CH_4 emission from ammonia utilization and untreated manure, as well as CO_2 emission from a large reliance on fossil fuels and traditional biomass, and anaerobic digestion as a biological waste treatment, technology to integrate the energy system and agricultural system into a manure management system has now attracted attention from the public. Of special concern in this task is the setting up of a manure-biogas-digestate model and evaluating its greenhouse gas (GHG) emission abatement compared to a reference system. Due to differences in livestock production, energy consumption pattern and agricultural land distribution, household biogas systems and livestock farm-based biogas systems are encouraged strongly in suburban and rural areas in China, respectively (Liu, 2010).

The aims of this chapter are to assess the environmental benefits from a manure treatment perspective, energy perspective and agricultural perspective of the entire biogas system and to analyze whether biogas system implementation is a good choice to achieve sustainability. Three steps are in focus to achieve the research aim: (1) Calculating GHG emission abatement from household biogas systems in rural areas and assessing which contributes to environmental impacts; (2) Assessment of environmental impact made through comparison between energy-environmental biogas systems and energy-ecological biogas systems; (3) Comparisons of these two types of manure-biogas-digestate systems with changes of energy consumption pattern and agricultural land area are then made. Through investigation of a household biogas project in western China and a livestock farm-based biogas project in east, the basic data used for assessing environmental benefits of the two systems were collected. In the household biogas system, CO_2 emission abatement is the largest in biogas substitution but CH_4 is produced in large amount from an uncovered

anaerobic lagoon after anaerobic digestion (AD). As for livestock farm-based biogas systems, AD selection and manure treatment process design play an important role in the GHG emission mitigation potential, which are based on the main purpose of project implementation. Both energy substitution and agricultural land acceptable capacity are considered as constraint conditions of large-scale biogas system development (Liu, 2010).

4.1.3 *Municipal and industrial waste*

The municipal solid waste (MSW) in China has increased at a rate of 8–10% in recent years (Bie *et al.*, 2007) due to the fast growth of the economy. It is expected by the REDP project (2005) that 210 million tonnes of MSW can be used in 2020 for methane production. Recently, the use of waste oil for biodiesel is very popular especially in south China. However, lack of accessible resources significantly blocks the further development of the biodiesel industry. Meanwhile, some other ways of using MSW for energy were analyzed in 2005 (Li *et al.*, 2005) and using MSW for landfill gas (LFG) was considered as having great potential.

China Industrial Waste Management, Inc. is well positioned to serve this market need as a comprehensive environmental services and solutions provider. For example, recently an energy efficiency center has been established in Dalian to provide our customers with consulting services, such as energy auditing of buildings and industrial plants, energy management programs, municipal energy efficiency planning, and other related services.

China Industrial Waste Management, Inc. is engaged in the collection, treatment, disposal and recycling of industrial wastes principally in Dalian and surrounding areas in Liaoning Province, People's Republic of China through its 90%-owned subsidiary Dalian Dongtai Industrial Waste Treatment Co., Ltd. ("Dongtai") and other indirect subsidiaries. Dongtai treats, disposes of and/or recycles many types of industrial wastes, and recycled waste products used by customers as raw material to produce chemical and metallurgy products. In addition, Dongtai treats or disposes of industrial waste through incineration, burial or water treatment, and provides environmental protection services, technology consultation, pollution treatment services, waste management design processing services, waste disposal solutions, waste transportation services, onsite waste management services, and environmental pollution remediation services.

China is the world's largest producer of MSW, producing over 223 million tonnes in 2008, and this is growing by 8–10% annually. The country produced 1.9 billion tonnes of industrial waste in 2008, an 8.3% increase from 2007, and of which 13.6 million tonnes were classified as hazardous waste. The predominant method of treatment is disposal by landfill, which accounts for about 80% of total treated MSW, followed by incineration and composting. However, faced with problems with upgrading landfills, most cities' landfills in China are not categorized as sanitary, with less than 10% meeting international standards. Thus, the key direction for many cities is incineration, especially for cities, which are more economically developed and have more capital to build incineration facilities, especially on the east coast.

4.1.4 *Wood processing remainders*

Currently, over 3 million hectares of firewood forest is available in China, thus acquiring 80 to 100 million tonnes biomass with high heating value. As for shrub forest, it covers the area of over 45 million hectares. Firewood forest, shrub harvest and forest greenery may produce 0.1 billion tonnes biomass, thus offering 0.3 billion tonne biomass fuel in the forest industry alone.

4.2 CO-COMBUSTION IN CHINA

4.2.1 *Introduction*

Biomass is one of the most important renewable energy resources. The amount of agriculture waste is about 700 million tonnes per year in China. It was assumed that about 50% of the

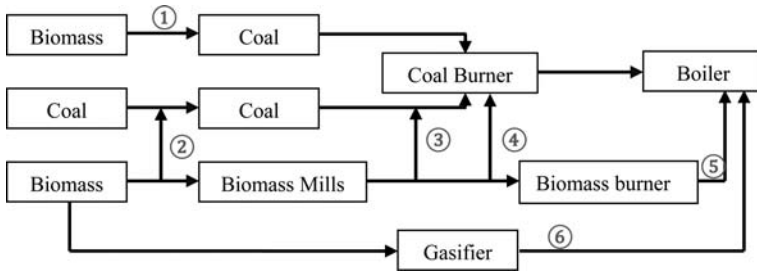


Figure 4.1. Six different co-combustion methods.

agriculture waste can be used as energy, for power generation, heat supply and cooking. It is scheduled that biomass power generation capacity in China will reach 3000 MW in 2020.

Biomass thermal conversion technology is commonly classified as combustion (direct combustion, co-combustion), gasification, pyrolysis, carbonization, and so on. Biomass utilization is regarded as a CO₂-neutral process. It is beneficial for continuous supply of energy and environmental protection.

4.2.2 Methods and technologies

Biomass co-combustion is known as the ‘partial substitution of coal (or other fossil fuel)’ with biomass in one process. Typical co-combustion power plant capacity is in the electrical output range of 50 MW to 700 MW in Denmark, Belgium, Poland, UK, etc. Co-combustion can be applied in existing coal equipped with pulverized coal firing systems or fluidized bed combustion systems or a gas fired power station where the fraction of biomass is up to 20% of the total fuel weight or energy consumption (VGB, 2008). Biomass co-combustion offers renewable energy with the lowest capital cost.

There are six types of biomass co-combustion methods as listed in Figure 4.1 (Livingston *et al.*, 2011). Number 1 is the milling of biomass (pellets) through modified coal mills, number 2 is the pre-mixing of the biomass with the coal, then the mixed fuel is milled and fired through the existing coal firing system, number 3 is the direct injection of pre-milled biomass into the pulverized coal running piping, number 4 is the direct injection of pre-milled biomass into modified coal burners or directly into the furnace, number 5 is the direct injection of the pre-milled biomass through dedicated biomass burners and number 6 is the biomass gasification gas, which is burned with coal in the boiler.

In summary, it is possible to distinguish the application of biomass in coal-fired power plants with three different biomass co-combustion concepts, which are shown as following (EUBIA, 2007; VGB, 2008; Tillman *et al.*, 2000; Brouwer *et al.*, 1995; Swanekamp *et al.*, 1995; Surmen *et al.*, 2003; Hunt *et al.*, 1997)

- **Direct co-combustion:** Direct co-combustion is the cheapest option, and the most straightforward and commonly applied approach. Biomass and coal are burned in the same boiler or gasifier, using the same or separate mills and burners, principally depending on the biomass fuel characteristics. Coal and biomass can be mixed before milling, or fed and milled by separated supply chains.
- **Indirect co-combustion:** Biomass is gasified and the product gas is then co-combusted in the main boiler. In a gasifier, the solid biomass is converted into a product gas and burned in the coal boiler. Sometimes the gas has to be cooled and cleaned, which is more challenging and implies higher operation costs. However, this approach offers a high degree of fuel flexibility.
- **Parallel co-combustion:** It is also possible to install a completely separate biomass boiler and utilize the steam in the existing coal power plant. The biomass is burnt in a separate boiler for

steam generation. The steam is used in the power plant together with the main steam. Parallel co-combustion is very popular in the pulp and paper industries as dedicated biomass boilers are used for the utilization of bark and waste wood. These industries economize and increase their energy efficiency by using the bio-residues and by-products from their main focus, the production of paper.

4.2.3 Advantages and disadvantages

Co-combustion in large-scale power plants can lead to an overall saving of fuels in comparison to independent fossil- and biomass-fired plants. Also, it can increase the fuel flexibility and reduce investment cost. Comparing with coal, biomass is a renewable energy source, which is considered as a CO₂-neutral fuel with lower emissions of SO₂, NO_x, heavy metals. NO_x emissions could be reduced by biomass, which has a low nitrogen and high volatile content. (EUBIA, 2007; Zhang *et al.*, 2010; Fu *et al.*, 2009; Daniele *et al.*, 2007). The co-combustion of coal and biomass has many advantages which can be described as follows (EUBIA, 2007; VGB, 2008):

1. Reducing greenhouse gases emission – biomass is considered as a ‘carbon neutral’ fuel in that the CO₂ emitted during biomass combustion is equal to that absorbed during the biomass growing. When biomass displaces a fossil fuel, a net reduction in greenhouse gas emissions is achieved.
2. Reducing local air pollutant emissions – burning biomass instead of fossil fuel results in lower emissions of SO₂ and NO_x.
3. Increasing electrical efficiency – the electrical efficiency of co-combustion power plant is higher than the traditional biomass plant, which has a small scale.
4. Ensuring security of supply – there exists a wide range of usable biomass fuels. Varying qualities and quantities of fuels can be partially compensated by adjusting the co-combustion rate.
5. Reducing cost – co-combustion presents the opportunity to use the existing fossil-fuel fired power plant infrastructure, which can be modified for co-combustion relatively easily. An optimum thermal biomass blending ratio of biomass co-combustion is 10% (on an energy basis) (Munir *et al.*, 2010). Addition of biomass to a coal-fired boiler does not impact or at worst only slightly decreases the overall generation efficiency of a coal-fired power plant. Compared with other renewable options, biomass co-firing represents the most cost-effective means of renewable power generation in many cases (Belošević *et al.*, 2010; Baxter *et al.*, 2005; Hein *et al.*, 1998).

Meanwhile, co-combustion of coal and biomass has some disadvantages shown as follows (VGB, 2008):

1. Preprocess – A fuel handling system is designed for a particular water content, size distribution, dust etc. With co-combustion of biomass it is necessary to adapt the existing or even build a new combustion system for that fuel.
2. Corrosion – Higher corrosion risk due to increased HCl formation in case of substitution of fuels with higher chlorine content (sewage sludge, some cereals). Many biomass fuels contain large amounts of alkalines, especially potassium, which may aggravate the fouling problems (Baxter *et al.*, 1993; Bakker *et al.*, 1997; Robinsin *et al.*, 2001a,b; Dunaway *et al.*, 2003; Lokare *et al.*, 2003).
3. A SCR DeNO_x catalyst can be blocked by ash particles or deactivated by potassium, chlorine, and in case of sewage sludge also poisoned by some heavy metals and metalloids (As, Zn).
4. Operating costs are typically higher for biomass than for coal. The most sensitive factor is the fuel cost. Even if the fuel is nominally free at the point of its generation (as many residues are), its transportation, preparation and on-site handling typically increase its effective cost per unit energy such that it rivals and sometimes exceeds that of coal.

For the utilization of the ash in the cement and concrete industry, the concentrations of alkali metals, P_2O_5 , SO_3 , Cl and unburned carbon in the ash are the critical parameters. It was found that the ashing temperature should be selected according to the biomasses proportion, when the biomass fraction is raised, the ash fusing temperature of blends decreases generally, and biomass with high P and K content proportion should not exceed 10% in co-firing (Dong *et al.*, 2010).

4.2.4 Research status

4.2.4.1 Different biomass for co-combustion

Biomass includes forest wastes, agricultural wastes, animal wastes and anthropomorphic wastes. Considering co-combustion with straw and coal could achieve large-scale and efficient utilization, it is attracting more and more attention and research. Most methods for research are concentrated in the laboratory using thermal gravimetric analysis, or measuring the combustion characteristics of mixtures of pollutants (including toxic gases and heavy metals, etc.) emission characteristics and ash melting characteristics through combustion or pyrolysis of different coals and biomass. The conclusions gained through these methods are an important reference for the design calculations and material choices of biomass-fired boilers, but the site condition is quite different from the experimental condition.

(1) Co-combustion of coal and agricultural wastes

In the Northeast Institute of Electric Power Engineering, experimental research on co-combustion of coal and corn stalk were carried out (Lu *et al.*, 2005). The results showed that the co-combustion of coal and corn stalk was helpful for coal burnout. With the increase of co-combustion rate from 20% to 80% (mass biomass to coal ratio), the burnout efficiency was increased, the burnout time was shortened and the burnout temperature was decreased. In Shandong University, Zhang *et al.* (2006) researched on the characteristics of straw co-combustion with coal by the thermal gravimetric analysis method. Cotton stalk, cornstalk, wheat-straw were chosen for co-combustion with coal at different heating rate (30, 50, 75 and 100 K/min) and different co-combustion rate (1:20, 1:10, 3:20, 1:5, 1:4, 3:10). The results showed that the co-combustion of coal and straw was helpful for coal burnout. With the rise of heating rate, the ignition temperature of straw mixed coal was decreased and the rate of combustion was increased.

In order to making clear the effect of the alkali metal K on nitrogen conversion in co-combustion of coal and straw, a series of experiments were carried by Yang *et al.* (2009). The results indicate that it is effective to inhibit the release of NO to add a certain proportion of straw. When the content of K increases in the de-ashed coal samples mixed with a low proportion of straw and KOH, it has a stronger catalytic effect on the reduction reaction of NO, and when the content of K reaches a certain value, the catalytic effect does not increase. The lower the O_2 content in the combustion atmosphere, the better the reduction of NO. Dong *et al.* (2010) have taken some experimental tests. The experiments were carried out at a 400 t/h power station boiler to test its economy and emission characteristics. Considering each operation controllable factor, the best running condition were optimized, which could keep better economy and emission performance. The optimized condition consisted of oxygen content 3.6%, combustion temperature 1278K, pulverized coal fineness $R_{90} = 20\%$, straw particle size 15 mm, primary air with average coordination, secondary air with waist type, and co-combustion ratio 20% (a heat ratio value).

(2) Co-combustion coal and MSW

Municipal solid waste (MSW), commonly known as trash or garbage (US), refuse or rubbish (UK) is a waste type consisting of everyday items we consume and discard. It predominantly includes food wastes, home yard wastes, containers and product packaging, and other miscellaneous inorganic wastes from residential, commercial, institutional, and industrial sources. Consequently, disposal of these MSW has become a serious problem which China is currently confronting.

In 2010, the volume of garbage disposal in China was 158.048 million tonnes. By the end of 2010, the number of treatment plants/grounds in China was 628, the treatment capacity (tonne/day)

Table 4.2. Volume of garbage disposal and treatment plants in China (2010).

Region	Area under cleaning program 10000 m ²	Volume of garbage disposal 10000 tonnes	Number of treatment plants/grounds unit	Sanitary landfill	Compost	Burning
National total	485033	15804.8	628	498	11	104
Beijing	13804	633	20	15	3	2
Tianjin	7322	183.7	8	6		2
Hebei	20050	589.3	26	20		4
Shanxi	10609	361.2	17	14		3
Inner Mongolia	9674	334	18	17	1	
Liaoning	28122	837.3	25	24	1	
Jilin	13037	499.4	7	5		2
Heilongjiang	14937	782.4	20	17		2
Shanghai	15879	732	12	4	2	3
Jiangsu	44088	1017.1	44	30		14
Zhejiang	27805	959	52	30		22
Anhui	17339	435.3	16	13		3
Fujian	11433	417.3	20	14		6
Jiangxi	9911	284	13	13		
Shandong	48528	992	55	46		8
Henan	20892	694.6	38	35	1	2
Hubei	16941	711.1	23	21		1
Hunan	12331	505.2	21	21		
Guangdong	62768	1938.6	41	25		16
Guangxi	11005	245.1	20	16	1	3
Hainan	4076	97.7	3	2		1
Chongqing	6136	256.7	13	12		1
Sichuan	15173	656	30	23		5
Guizhou	3405	213.3	12	12		
Yunnan	9726	265.5	19	12	2	3
Tibet	539	16.3				
Shaanxi	10546	388.3	15	11		1
Gansu	5816	278.3	13	13		
Qinghai	1951	86.3	3	3		
Ningxia	3347	91.9	7	7		
Xinjiang	7843	303.3	17	17		

Note: Data from National Bureau of Statistics of China.

is 0.3876 million tonnes, the proportion of treated garbage (%) is 77.9%, all which are shown at Table 4.2, Table 4.3 and Table 4.4.

As shown in Figure 4.2, garbage disposed by burning isn't the most important way in China, which takes 22% and less than other disposing ways e.g. sanitary landfill. Incineration is a waste treatment process that involves the combustion of organic substances contained in waste materials (Andrew, 2005). Incineration can reduce the solid mass of the original waste by 80–85% and the volume (already compressed somewhat in garbage trucks) by 95–96%, depending on composition and degree of recovery of materials such as metals from the ash for recycling (Ramboll, 2006).

In China, researchers have focused on co-incineration performance tests and experiments of coal and different types of MSW. Gu *et al.* (2003) focused on the co-combustion research of municipal sewage sludge and coal. With a thermogravimetric method, the research results showed that co-combustion could enhance activation energy with a lowering of the ignition temperature.

Table 4.3. Quantity of waste treated in China (2010) (Unit: million tonnes).

Region	Quantity of waste treated	Sanitary landfill	Compost	Burning	City sanitation special vehicles (unit)
National total	12317.8	9598.3	180.8	2316.7	90414
Beijing	613.7	445.4	79.3	89.1	7461
Tianjin	183.7	125.4		58.3	1951
Hebei	411.5	311.6		58.9	3306
Shanxi	265.8	213.5		52.3	3689
Inner Mongolia	276.5	251.7	24.9		1480
Liaoning	593.5	571.6	21.9		4998
Jilin	222.3	172.4		49.9	2608
Heilongjiang	315.7	284.6		16.6	3814
Shanghai	599.2	416.5	21.2	108.1	5560
Jiangsu	951.7	488.5		458.7	7481
Zhejiang	942.7	504.9		437.8	4685
Anhui	281	231.1		49.9	1508
Fujian	383.8	241.7		142	2036
Jiangxi	243.9	243.9			899
Shandong	911.6	751.9		131.4	5983
Henan	573.7	501	6.9	65.7	3025
Hubei	436.9	405.8		18.4	3077
Hunan	399.1	399.1			1998
Guangdong	1398	1031.6		366.4	8535
Guangxi	223.3	203.5	9.3	10.5	1748
Hainan	66.4	61.6		4.8	1525
Chongqing	253.7	216.3		37.4	1786
Sichuan	569.8	464.3	7	80.8	3301
Guizhou	193.3	193.3			882
Yunnan	234.4	123.2	10.4	77.7	1783
Tibet					20
Shaanxi	310	281.2		2.2	1719
Gansu	105.6	105.6			1045
Qinghai	58.1	58.1			330
Ningxia	85	85			554
Xinjiang	214	214			1627

Note: Data from National Bureau of Statistics of China.

The fuels have basically attained devolatilization characteristics in the co-combustion process. Liu's (2006) experimental research showed that the reactivity of the blend with 20 wt. % of sludge is similar to that of coal. When the blend is with 50 wt. %, there are two temperature zones with obviously different reactivity trends. In the lower temperature zone (less than 430°C), the reactivity of the blend is similar to that of the sludge, and in the higher temperature zone (greater than 430°C), the reactivity of the blend is close to that of the coal. Zhao *et al.* (2005) researched on co-combustion of sludge/residue in a paper mill with high moisture content and low heating value coal at the hot circulating fluidized bed test facility. His research showed that when the secondary air rate increases, temperature in the dense bed decreased slightly and temperature in the dilute phase region declined, while the combustion efficiency was increased. When the excess air coefficient was increased, temperature in the dense bed increased, temperature in the dilute phase region increased at first and then declined forming an optimum value corresponding to the highest combustion efficiency. When the ratio of paper mill waste to coal was increased, the decline in temperatures in both dense bed and dilute phase region was decreased, and the combustion efficiency was decreased. Lu *et al.* (2004a) indicated that co-combustion of sewage

Table 4.4. The waste treatment capacity (tonne/day) in China (2010).

Region	Treatment capacity (tonne/day)	Sanitary landfill	Compost	Burning	Proportion of treated garbage (%)
National total	387607	289957	5480	84940	77.9
Beijing	16680	12080	2400	2200	97
Tianjin	8000	6200		1800	100
Hebei	13614	10064		2450	69.8
Shanxi	10568	7968		2600	73.6
Inner Mongolia	9167	8367	800		82.8
Liaoning	17247	16647	600		70.9
Jilin	6496	4456		2040	44.5
Heilongjiang	10969	9869		500	40.4
Shanghai	10545	5750	520	2575	81.9
Jiangsu	37637	22445		15192	93.6
Zhejiang	33323	16438		16885	98.3
Anhui	9420	7670		1750	64.6
Fujian	12747	7197		5550	92
Jiangxi	6066	6066			85.9
Shandong	35225	26425		8200	91.9
Henan	20416	17616	400	2400	82.6
Hubei	12800	11400		1000	61.4
Hunan	11818	11818			79
Guangdong	33956	22213		11743	72.1
Guangxi	8191	6871	400	920	91.1
Hainan	1764	1539		225	68
Chongqing	6465	5265		1200	98.8
Sichuan	16974	13334		2340	86.9
Guizhou	5697	5697			90.6
Yunnan	7749	3849	360	2870	88.3
Tibet					
Shaanxi	10707	9347		500	79.8
Gansu	3355	3355			38
Qinghai	931	931			67.3
Ningxia	2785	2785			92.5
Xinjiang	6295	6295			70.6

Note: Data from National Bureau of Statistics of China.

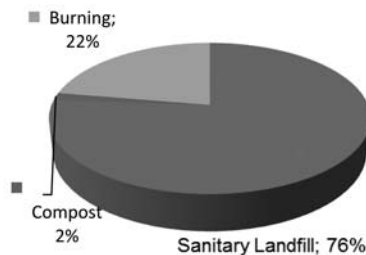


Figure 4.2. Percentage of different garbage disposal methods in China (2010).

sludge with coal on a circulating fluidized bed was stable at water contents of 30–60% in sewage sludge and co-combustion rates of 25–100%.

Co-combustion of coal and refuse derived fuel (RDF) were carried out in a bubbling fluidized bed combustor by Sun *et al.* (2006). The feasibility of solidification and co-combustion of waste

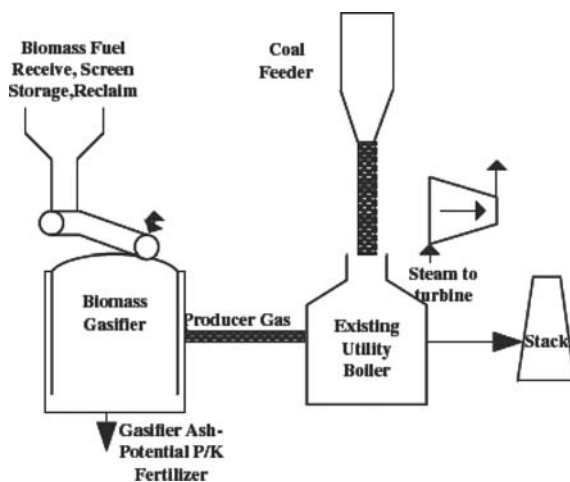


Figure 4.3. Biomass co-combustion system.

products in oily wastewater with coal was analyzed by Liu *et al.* (2005). The combustion process, ignition and burnout characteristics of waste tire and coal with a tire-coal ratio of 10%, 30% and 50% were investigated by means of thermogravimetric analysis (TGA), which were carried out by Li *et al.* (2007), whose research showed that co-combustion with waste tires could improve the burnout characteristics. Co-combustion of waste plastic and coal in fluidized bed were researched by Jin *et al.* (2001) and co-combustion of Medical Solid Waste and coal in a CFBC by Pu Ge *et al.* (2003).

4.2.4.2 Biomass gasification gas for co-combustion

Biomass gasification gas is used as a way of co-combustion so that biomass is converted into combustible gas, and then sent into the boiler. Biomass gasification gas is rich in H_2 , CH_4 and CO etc. with low ash content, very low sulfur content. It is an ideal co-combustion fuel and effective to decrease the emissions of nitrogen oxides.

The co-combustion based biomass gasification can avoid most of the problems associated with direct co-combustion, such as boiler fouling, corrosion, and ash characteristics altering. As shown in Figure 4.3, biomass was gasified in a gasifier and the product gas was fed into a coal fired boiler for co-combustion. The technical economical feasibility of co-combustion with biomass gasification has been verified. The most important thing was to make clear the possible effect of co-combustion on burnout, emissions and what retrofit work should be done. Therefore, a CFD modeling study of coal and product gas (from biomass gasification) co-combustion was carried out Dong *et al.* (2010).

In the study, 14% by heat basis of product gas from biomass gasification was injected from the lowest layer burner and co-fired with coal in a 600 MW tangential PC boiler in Yuan Baoshan power plant (China). Figure 4.4 shows a sketch of the Yuan Baoshan Boiler. The size of the boiler is 20.1 m (deep) $\times$ 20 m (wide) $\times$ 73.9 m (high). The burner is a tangential swinging burner with size of 0.747 m (wide) $\times$ 0.838 m (high). There were eight layers of burners and six layers of secondary air inlets. The designed coal was Yuanbaoshan lignite.

The simulation results showed that: (1) The combustion temperature in the furnace was lower and the flue gas volume was higher for co-combustion cases. The convection heat transfer area should be increased or the co-combustion ratio of product gas to coal should be limited to keep the rated capacity. (2) NO emission was reduced about 50–70% when the product gas was injected

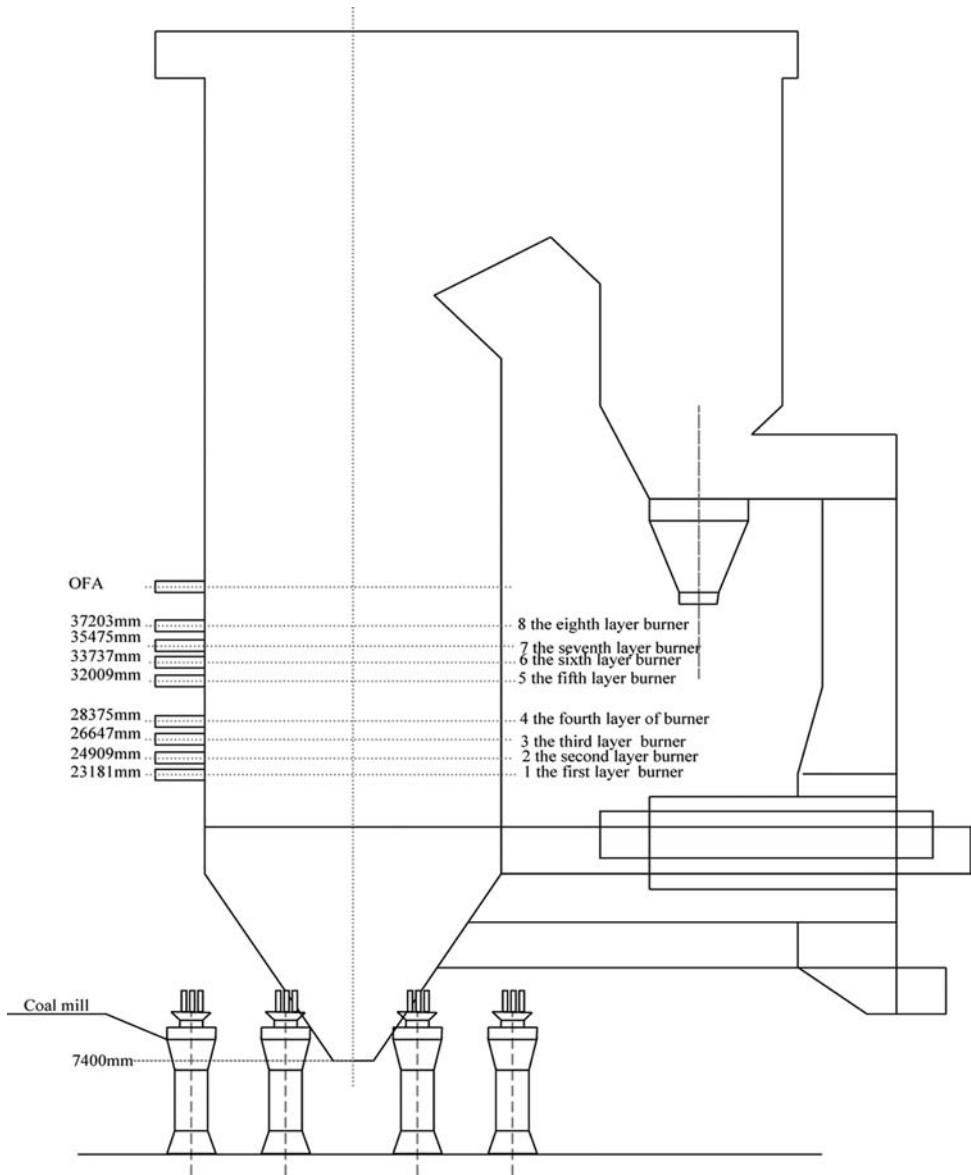


Figure 4.4. A sketch of the Yuan Baoshan Boiler.

through the lowest layer burner. The NO emission also depended on the burner design and operation level. (3) The fouling problem caused by high temperatures can be reduced for the lower co-combustion temperature.

The biomass gasification and co-combustion process has been studied by Huang (2011). A model of co-combustion of coal and biomass-gas was established focusing on the research of co-combustion power generation of corn stalk gasification gas and coal. Based on the first and the second law of thermodynamics, co-combustion with corn stalk gasification gas 5% was analyzed. In the research process, an exergy flow graph of the boiler in co-combustion is shown in Figure 4.5. Comparing with pure coal burning, the research of co-combustion (5–30%

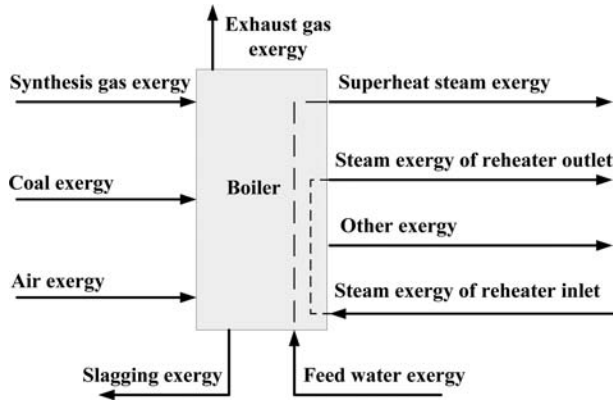


Figure 4.5. Exergy flow graph of boiler in co-combustion.

Table 4.5. Heat efficiency, exergy efficiency, theoretical burned gas mass flow and theoretical air mass flow vs. the change of co-combustion ratios.

Co-combustion rate (%)	0	5	10	15	20	25	30
Thermal efficiency (%)	92	91.97	91.95	91.92	91.89	91.87	91.84
Exergy efficiency (%)	51.27	51.25	51.23	51.21	51.18	51.16	51.13
Theoretical quantity of flue gas (ten thousand m ³ /h)	75.97	76.73	77.48	78.24	79.00	79.75	80.51
Theoretical quantity of air (ten thousand m ³ /h)	69.52	68.75	67.99	67.23	66.47	65.71	64.94

biomass-gas) shows that the theoretical burned gas mass flow will reduce and the theoretical air mass flow will increase and both boiler heat efficiency and exergy efficiency will decrease when there is more biomass gas co-combustion, which was shown at Table 4.5.

Dong (2011) modeled the co-combustion integrated system, which combined a biomass gasification system and a 300 MW circulating fluidized bed boiler system, as shown in Figure 4.6. The optimized gasification gas is sent into the boiler with the temperature 598°C heating value 5401 kJ/Nm³ and gasification efficiency 72.25%. The results reveal that with increase of the co-combustion rate, theoretical air volume decreases, fuel gas volume increases, combustion temperature and exhaust gas temperature increase, boiler efficiency decreases. Adding some heating surfaces at backpass should be used to improve boiler efficiency. The simulation results are shown in Figure 4.7.

Figure 4.7 shows the influence of reburning ratio on furnace temperature, flue gas temperature and boiler efficiency. The average temperature of the furnace was proportional to the biomass gasification gas. When the reburning ratio was increased from 0 to 20%, the furnace temperature went up from 840 to 872°C. Given that the total heat value of biomass gas and coal is invariable, the average furnace temperature was rising because the temperature of biomass gas injected was 598°C. When the reburning ratio was increased from 0 to 20%, exhaust temperature also grew from 137.2 to 176.2°C, which agreed with the change of furnace temperature.

When the reburning ratio was increased from 0 to 20%, boiler efficiency reduced from 93.8 to 91.3%. It can be inferred from Figure 4.7 that the flue gas temperature and heat losses of exhaust were proportional to the biomass reburning ratio. The boiler efficiency was inversely proportional to the biomass reburning ratio.

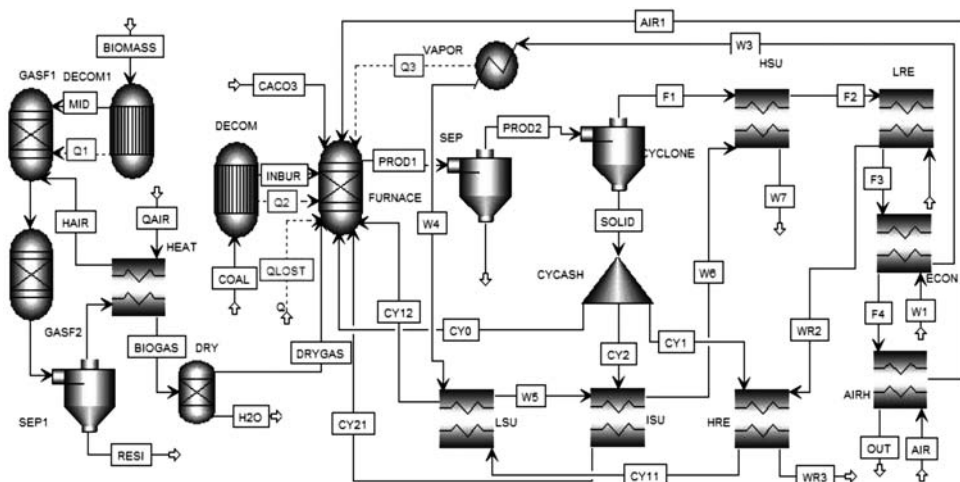


Figure 4.6. The integrated system of biomass gasification and circulating fluidized bed boiler.

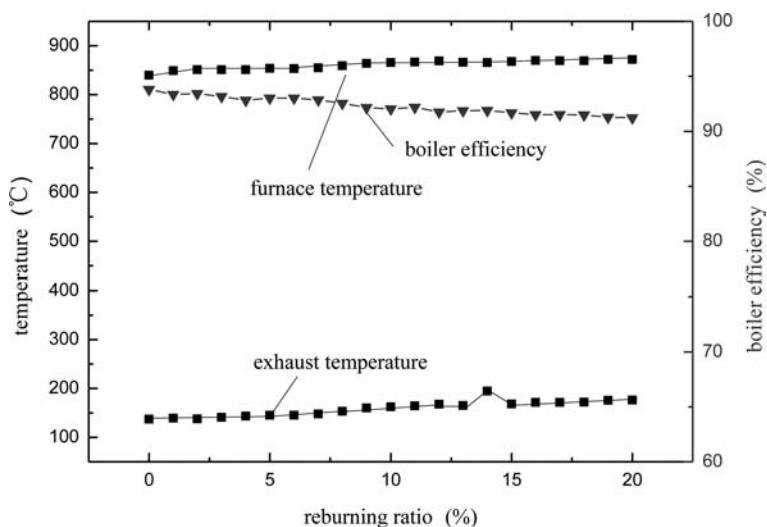


Figure 4.7. Influence of reburning ratio on furnace temperature, flue gas temperature and boiler efficiency.

The technology of large coal-fired units is mature and it has a high power generation efficiency, so the integration of straw gasification and coal-fired power generation can take the advantage of increasing the efficiency and reducing cost of electricity. In Europe and United States, the technology has some commercial applications, and has become a new efficient way of reducing greenhouse gas emissions. The gasifier is the key equipment for straw gasification and coal-fired power generation, which at the operating level has a large impact on the effect of straw utilization.

4.2.4.3 Pollutant emissions from co-combustion

Comparing with coal, burning biomass results in lower levels of SO_x . Some straw has no sulfur content, which could decrease the SO_x emission with co-combustion coal and biomass.

NO_x emissions may increase, decrease, or remain the same, depending on the fuel, combustion condition and operating conditions (Baxter, 2005).

4.2.4.3.1 The influence of solid biomass fuel

During co-combustion of coal and solid biomass fuel, biomass went through four stages, namely dehydration, biomass pyrolytic and volatile burning, the combustion and solid carbon of volatile surface burning coexisting, and solid carbon burning at the surface. Many products of these stages have a reducibility on NO_x.

Based on a small drop-tube furnace, it is shown that 50–70% of NO emissions could be reduced using wood chips, orange peel, and rice husk as the co-combustion fuels (Li *et al.*, 2004). An experimental study on the biomass co-combustion in a multi-function test-bed was carried out by Cheng *et al.* (2007). The influence of the fuel properties, the operation parameters (fuel particle size, and fuel ratio) and operation parameters (co-combustion zone temperature, excess air coefficient, residence time, initial NO concentration) on biomass co-combustion were researched with wheat straw and corn stalk, peanut shell and sawdust as biomass material. The effect of biomass co-combustion on the reduction of NO emissions was similar as pulverized coal burning.

Han *et al.* (2008) studied biomass co-combustion for reduction of NO_x and indicated that the performance order of reducing NO_x is: wheat straw, peanut shells, and sawdust. The appropriate condition were co-combustion temperature of 950 to 1050°C, co-combustion rate of 15 to 25%, excess air rate of 0.6 to 0.8, and residence time of 1s.

Yang *et al.* (2009) researched the influence of alkali metal K on nitrogen conversion in co-combustion of coal and straw. They showed that a certain proportion of straw in the deashed samples is effective to control NO emissions. The formation rate of NO was changed from one peak to two peaks with the proportion of straw increased in TG. Increasing K from 0 to 3% in the samples mixed with a proportion of straw at 50% and a proportion of KOH at 25%, has the strongest catalytic effect on the reduction reaction of NO. When the K reaches a certain value, the catalytic effect was stable. The lower the O₂ content was in the co-combustion condition, the better the reduction reaction of NO.

4.2.4.3.2 The influence of biomass gasification gas

Considering the advantages of indirect co-combustion technology, many researchers focused on the reduction of NO_x emissions with co-combustion coal and biomass gasification gas.

Fan *et al.* (2006) performed experiments with simulated biomass gasification gas (CO/H₂/CH₄/C₃H₆) and found that the reduction effect on NO emissions was decreased with the concentration of H₂, CO in biomass gas increased; the proportion of CH₄, C₂H₆, C₂H₄ increased, the NO reduction efficiency increased, where the reaction $\text{CH}_i + \text{NO} \rightarrow \text{N}_2 + \text{M}$ played a leading role.

Duan *et al.* (2006), performed experiments with simulated biomass gasification gas (CO/CO₂/CH₄/H₂/N₂) co-combustion for reduction of NO in an electrical heating corundum tube flow reactor. It is confirmed that the mixing of biomass gasification gas can improve NO reduction rate when the oxygen content changed in a range of 0–5% in reactor entrance, temperature changed from 1000 to 1400°C

Dong and Hu *et al.* (2009) performed some experiments to study the influence biomass simulation gas played on emissions of N₂O in a small fluidized bed reactor. Also, N₂O reduction was effected by the co-combustion ratio of biomass gas (0–1.4%), co-combustion temperature (800–1000°C), residence time in co-combustion zone (0.16–0.32 s), O₂ initial concentration of gas (4–8%), bed material height (0–50 mm), and other conditions changed. The results showed that the higher the co-combustion temperature was, the higher the thermal decomposition rate of N₂O was. With the biomass gas content of 1.0%, when the co-combustion temperature was 850°C, N₂O decomposed absolutely; the oxygen concentration of flue gas plays an inhibitory action on N₂O decomposition, but the injection of biomass gas can effectively avoid this problem. Based on

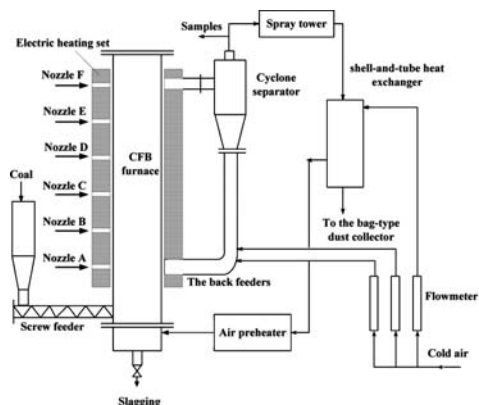
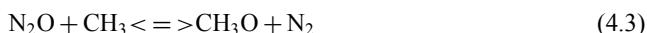
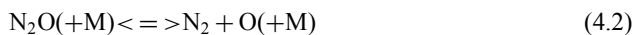


Figure 4.8. Circulating fluidized bed system.

this, the further research showed that in the process of biomass gas reducing N_2O , the following reactions took the more important influence on N_2O decomposition:



An integrated system, including a circulating fluidized bed subsystem and a fixed bed biomass gasifier subsystem, was built by Zhang (2011). The circulating fluidized bed subsystem mainly includes a circulating fluidized bed reactor, a hot air ceramic electric heater, a fluidized bed start heating furnace, a spiral feeder, a spray desuperheating tower, a tubular heat exchanger and a mechanical vibration type bag dust extraction, which is shown in Figure 4.8. In order to describe different nozzles, R_h is defined as the ratio of its height away from air distributor to the furnace diameter. Corresponding to nozzle A, B, C, D, E and F, the value of R_h was 4.3, 6.3, 8.3, 10.3, 12.3 and 14.3 respectively. Six temperature probes were distributed at the nozzles.

Figure 4.9 is the flow diagram and photograph of the fixed bed biomass gasification subsystem, which mainly includes fixed bed gasifier, catalytic tower, spraying tower, purification tower, water ring type vacuum pump, drying tower and connection pipes. Rice husk, the raw material for gasification, was fed into the gasifier from the hopper. The produced gas flowed into the catalyzing tower from the bottom of the gasifier. Some activated carbon particles were added to the catalyzing tower for adsorbing and catalyzing decomposition of the tar produced. Then the gases were purified further through the water tower for protecting other equipments and pipes, and were dried by the drying tower with a water-ring vacuum pump. Finally, the dried gas was used for co-firing with coal in the circulating fluidized bed, which helps to reduce N_2O and NO emissions. The air used in the gasifier was supplied from the medium of the gasifier at the top of the hopper. After gasification, the ash fell into the ash hopper at the bottom of the gasifier. At the end of experiments the ash was cleaned. During operating the pilot plant system, firstly the water ring vacuum pump is run before starting the gasifier system to ensure the gasifier system operated with a slightly negative pressure, and then starting the circulating water pump in the water tower. After checking all the relevant components, the gasifier was ignited with a electric igniting torch.

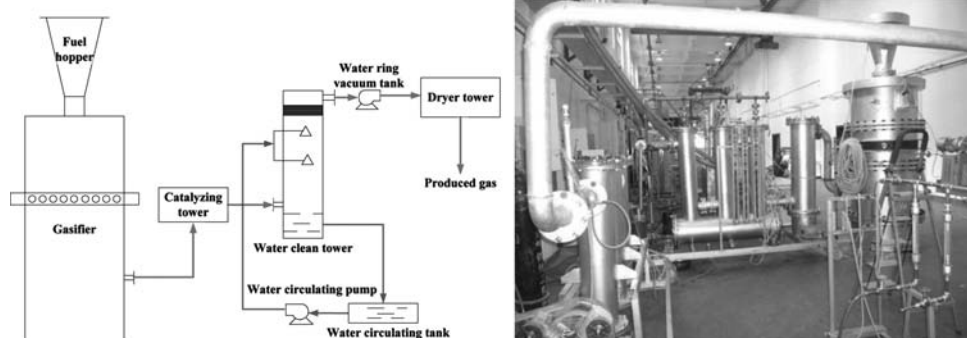


Figure 4.9. Process diagram of flue gas analysis.

From an analysis of the results, it is concluded that:

1. With the increase of the proportion of the reburning, the theoretical air requirement was decreased, and in contrast the theoretical flue gas was increased accordingly, as was the furnace temperature and exhaust temperature. However, the boiler efficiency was decreased with the increase of exhaust volume and exhaust temperature.
2. By injecting gasified biomass from the nozzle with a length to diameter ratio of 8.3, the highest N_2O removal rate of 99% was achieved, while its NO removal rate was 44%.

4.2.5 The applications of co-combustion in China

4.2.5.1 Chuang Municipality Lutang Sugar Factory

Chuang Municipality Lutang Sugar Factory of Guangxi province improved the boiler by using a 35 t/h fluidized bed boiler for burning a mixture of coal and bagasse instead of 25 t/h pulverized-coal fired boiler. With a ratio of coal to bagasse of 60 to 40%, the project was successful (Liu *et al.*, 2003).

Chuang Municipality Lutang Sugar Factory uses the fanlike coal pulverizer for milling in the 25 t/h pulverized coal fired boilers. The boilers are dual-drum transverse arrangement of convection bank boilers, the superheaters are arranged between slag screens with a convection bank, and economizers and air preheaters are arranged in the rear flue. Boiler design parameters: evaporation capacity of 25 t/h, vapor pressure of 2.4.5 MPa, vapor temperature of 400°C. The steam boilers produce is used to generate electricity and heating. The boilers need to burn high quality coal instead of bagasse, which is combustion by-product of virgin sugar. The boiler efficiency is not high, thus running a large consumption. Chuang Municipality Lutang Sugar Factory has an urgent requirement to transform the boilers, so that coal and bagasse can be mixed in the combustion to reduce the operating cost.

In order to expand the evaporation capacity (from 25 to 35 t/h) and mix coal with bagasse for combustion, the boilers use circulating fluid bed combustion, being a circulating fluid bed type of furnace with pipe laying. The boiler standards after transformation should be: (1) Fluidized bed boilers with coal mixed bagasse for fuel, the ratio of 60% for soft coal with 40% for bagasse. Net calorific power of soft coal is 16,747 kJ/kg, and volatile is 15.18%. (2) Boiler evaporation of 35 t/h. (3) Boiler steam with the same pressure and temperature. The detailed transformation of the boiler heating surface is shown in Table 4.6.

After the transformed boilers are put into operation, coal and bagasse are mixed to be burned (the ratio of 60% for soft coal with 40% for bagasse). Coal enters the combustion chamber through the belt feeder and bagasse enters the dilute-phase zone by pneumatic power. Coal main burns in the dense phase bed and bagasse main burns in the dilute phase bed. Evaporation capacity can

Table 4.6. Heating surface arrangement.

Heating surface	Heating surface after transformation (m ²) (35 t/h)	Heating surface before transformation (m ²) (25 t/h)
Pipe laying	29.6	0
Water screen	119.7	131.2
High temperature superheater	45.0	48.8
Low temperature superheater	112.2	125.8
Economizer	738.7	368.1
Air preheater	690.9	725.5

reach 30–32 t/h. Temperature under the bed is 930–980°C and at combustion chamber outlet is 680–720°. Boiler steam parameters can meet the design values and boilers run stable.

4.2.5.2 Fengxian XinYuan Biomass CHP Thermo Power Co., Ltd

According to the report named Post-evaluation by Case Study of Various Technical Solutions to Biomass (crop straw) Power Generation in Jiangsu, two models of co-combustion are introduced in the book. They are Fengxian XinYuan Biomass CHP Thermo Power Co., Ltd and Baoying Xiexin Biomass Power Co., Ltd.

Fengxian XinYuan Biomass CHP Thermo Power Co., Ltd in Xuzhou, was put into operation in 2003. The total investment of the project is 250 million Yuan, of which registered capital is 66 million Yuan. The project construction started in March 18, 2003. Scale in stage 1 covers an area of 220 mu (1 mu = 614 m²), using three 75 t/h sub-high temperature and sub-high pressure circulating fluidized bed boilers produced by Jinan boiler factory and two 15 MW extraction condensing turbo generator units and related auxiliary equipments produced by Nanjing turbine factories, in which units 1 and 2 respectively went into operation in October 17, 2003 and November 26, 2003 in way of co-generation.

Fengxian XinYuan uses two different kinds of fuels, biomass (renewable) and coal (non-renewable). Types of coal include coal, coal gangue and slime and so on. Biomass is mainly from rice husk, loose sawdust and compression molding sawdust. In addition, crushed poplar branches, fruit tree branches (Fengxian is rich in fruits such as apples and peaches), bark as well as forestry residues also can be used.

At present, the mixing ratio of biomass is approximately 20% (mass ratio) in this plant, where coal is still the main fuel. The co-combustion model establishes a good foundation for steady operation and reduces the risk of discontinuous supply of biomass fuels.

Biomass mixed to burn in Fengxian XinYuan is mainly rice husk and sawdust, which are particle fuels and can be directly put into furnace without pre-treatment.

The feeding process of the case is as follows: Biomass is delivered to the hopper first, then transported into the pipeline from the bottom of the hopper and next sent to the biomass and coal mixture room by “V”-shaped belt conveyor. The coal is from pipelines in the vertical direction of the biomass transportation pipeline. After mixing in the hopper, coal and biomass fall on the belt conveyor and then are sent to the storage bin and furnace.

The power plant adopts Combined Heat and Power (CHP) and supply heating mainly, power secondly, which is a thermal power plant of half-public welfare. Heat output of the plant in 2006 is 289,000 tonnes, which is mainly supplied to 15 to 16 enterprises of the industrial park in Fengxian, with price of steam 110 Yuan per tonne on average. The total generation capacity is 210 million kWh, of which net generation to grid is 189 million kWh (electricity consumption in the plant is 10%).

The mixed ratio of biomass in Fengxian XinYuan is 20% (mass ratio), which fails to meet the requirements of the country about the electricity subsidy enjoyed by co-combustion power

Table 4.7. Parameters of the thermal plant boiler.

Boiler type	AG-35/3.82 m
Design efficiency	87.7%
Fuel type	1#, 4# Bituminous coal ($Q_{net,v,av} = 18840.6 \text{ kJ/kg}$)
Combustion	Low magnification of circulating fluidized bed
Fly ash	External dual-cyclone separator
Manufacture date	1998.11
Exhaust gas temperature	130–160°C
Rated evaporation	35 t/h (After the transformation, the maximum output is 38 t/h)
Rated operating pressure	3.83 MPa
Rated steam temperature	450°C
Bed layout	Double bed/transverse buried pipe
Circulation ratio	3–4
Date of installation and use	2002.12
Production unit	Anshan Boiler Group Corp. Ltd.

plant (ratio of biomass accounted in total heating value of power generation consumption exceeds 80%), so they are unable to enjoy the subsidy of electricity price which is 0.25 Yuan/kWh.

4.2.5.3 Heilongjiang Jiansanjiang Heating and Power Plant

In Bureau of Heilongjiang Agricultural Reclamation Department Sanjiang Branch, a 35 t/h circulating fluidized bed boiler of a thermal power plant burns the mixture of coal and rice husk instead of burning the original bituminous coal. It was found that the boiler saves about 20–40% coal. In the boiler, nearly 200,000 m³ of straw were burned every year and saved the cost of coal about 2.1681 million Yuan (Wang, 2004). The branch has a rice planting area of about 1.6665 billion m², with a rice output of 1.25 million tonnes per year. The thermal power plant had done a lot of research work in how to utilize rice husk to combust mixed with raw coal. As a result, a new way was found that a small and medium-sized circulating fluidized bed boiler is used for producing heat and generating power with co-combustion of coal and rice husk. The information on the boiler is shown at Table 4.7.

In the plant, coal is conveyed piecewise with a belt. Rice husk is transported by air conveying, which is monitored automatically by limit switches.

Under a condition of the same coal and the same boiler output, comparing with pure coal, the boiler using co-combustion of coal and rice husk could save coal amount between 20–40% (average heat of coal $Q_{net,v,ar} = 18,924,135 \text{ kJ/kg}$). According to coal consumption of 6078 t/h with a boiler rated evaporation capacity of 35 t/h, it can be calculated and obtained that the average coal-saving amount is 1823 kg/h and the coal-saving amount is about 43.8 t/d (lower calorific value of rice husk, $Q_{net,v,ar} = 14,785 \text{ kJ/kg}$; density is 8–9.26 m³/t, the moisture content of rice husk is 12–18%). If the plant works 11 months per year, the coal-saving amount is 14,454 t. Annually it could save the cost of raw coal is 2.1681 million yuan with the average price of coal is 150 yuan/t. In environmental protection, the plant has burned nearly 200,000 m³ rice husk per year, which realizing the transformation of waste to treasure with significant social and environmental benefits.

4.2.5.4 Baoying Xiexin Biomass Power Co., Ltd

Baoying Xiexin Biomass Power Co., Ltd was put into operation in 2005. Baoying Xiexin Biomass Power Co., Ltd (hereinafter referred to as Baoying Xiexin) is located in Anyi industrial zone in Anyi town, of Baoying county in Yangzhou. It is an environmental Combined Heat and Power (CHP) enterprise invested to build by Hong Kong Xiexing group (Holding) Limited Company.

Main equipments (boiler, steam turbine unit, etc.) of the plant have been running steadily without any serious failures since units 1 and 2 were put into operation in 2005. There were some problems in unit 3 about the feed system and combustion system in the initial operation period. But through technicians' repeated debugging and exploration, the problems had been solved preliminarily and the plant could operate normally, which is a successful case of the co-combustion model.

Fuel is the key to ensure power plants operate continuously and steadily. The plant uses two different kinds of fuels, biomass (renewable) and coal (non-renewable). Non-renewable fuels include coal, peat and low quality coal.

The biomass used is not only the rice husk but also a large number of crop straws, rice straw, wheat straw and so on. It is worth noting that distribution and collection of rice husk and straw are completely different.

The mixed fuels are not only rice husk but also a large amount of rice straw, wheat straw and other soft straw in Baoying Xiexin. Fuel feeding is distinctive and the plant owns two sets of feeding systems, one of co-combustion and the other of direct combustion.

The feeding process of co-combustion is as follows: Boilers 1 and 2 share the same feeding system. Then the biomass fuels (mainly rice husk) are sent to respective feeding pipes by scraper conveyor and electric three-way valve, which can control the amount of feeding biomass simultaneously, and finally biomass together with coal are sent into the furnace.

Similar to the power plant in XinYuan Fengxian, this plant also adopts Combined Heat and Power, with power generation mainly and heating supplement secondly. In 2006, total power generation was 2.24 billion kWh and net generation to grid was 206 million kWh. Grid electricity price (tax included) was 0.646 Yuan/kWh and the plant sold the power to Jiangsu Electric Power Company.

Because mixing ratio of the plant satisfies the requirements, the plant received electricity price subsidy of 0.25 Yuan/kWh in November 2007. Net power price, including tax, is 0.646 Yuan/kWh at present, which was 0.469 Yuan/kWh before. At the same time, the name of the plant was changed from Baoying Xiexin Biomass Environmental Protection Thermoelectric Co., Ltd. to Baoying Xiexin Biomass Power Co., Ltd.

4.2.6 Shiliquan power plant

In China, the first co-combustion coal and straw system was operated successfully in Shiliquan power plant of Huadian Power International Co. LTD. in December 16, 2005. This was a important breakthrough in the field of biomass power generation in China.

The straw power generation technology of the Shiliquan power plant was introduced from Denmark, with which the number 5 boiler (140 MW) was optimized and integrated a 30 MW straw combustion system. In the system, purchase, stockpile, pulverization and conveying equipment for straw have been added, and at the same time two straw burners have been installed at the left and the right wall of the boiler. The air feed system and the associated control system have also been remolded, but the original boiler combustion system has not been altered. Keeping the performances and the parameters of the original boiler constant, the improved boiler can combust the mixture of pulverized coal and straw, also it could combust the pulverized coal alone. This is the first combustion for a power generation project using the mixture of straw and pulverized coal that is remolded on an old generating unit in China. If the generation unit runs for 7236 hours per year, it will consume more than 1.05 million tonnes of straw, which means 7.56 million tonnes of raw coal can be saved, whose thermal value is 5000 kcal/kg. This will bring the local peasants more than 30 million RMB per year. Compared with the coal power, the generating unit remolded by the straw power generation can reduce the sulfur dioxide exhaust by 1500 tonnes per year, it can also lighten the atmospheric pollution of harmful gas like carbon dioxide, carbon monoxide and the suspended particulate effectively, which are produced through combusting the straw by the peasants.

4.3 BIOMASS GASIFICATION IN CHINA

4.3.1 Introduction

Gasification is a technology commonly used nowadays for extracting energy from biomass. Over the past decade, there has been great progress in the development of gasification technology in China. Many kinds of biomass gasification processes have been developed, treating different materials for various purposes.

4.3.2 Gasification technology development

Dating back to the 19th century, gasification technology now attracts new interests in Europe, because of the end use flexibility of the syngas (Lan *et al.*, 2011).

A charcoal gasifier had been developed in the 1940s and was tried to drive vehicles with the technology, which is the initial exploration in China in gasification of biomass. But the technology did not obtain further development for various reasons.

A fluidized bed reactor for industrial applications had been developed in China in the 1950s, but there were some imperfections in the technology, and the application was suspended. In the 1960s, Chinese researchers began to study the biomass gasification power generation and gained some experiences, and the preliminary prototype had been developed and gained some experiences, but these researches were stopped because of the economic conditions and the small profits.

A fixed bed gasifier (updraft and downdraft) circulating fluidized bed gasifier was developed in China in the 1980s. The product gases were used for power generation, supplying heat and cooking.

An 1 MW BPGP system with a circulating fluidized bed (CFB) gasifier had been developed, and constructed in a rice mill in the Fujian province of China (Wu *et al.*, 2002; Wang *et al.*, 2005; Lu *et al.*, 2004b; Wu *et al.*, 2003). A neural network was focused on for the simulation of gasification process. An artificial neural network model was developed to simulate the gasification processes in order to obtain the gasification profiles (Guo *et al.*, 2001; Tang *et al.*, 2003; Wang *et al.*, 2002).

Gasification and polygeneration technology in the fluidized bed were concentrated on by Tie *et al.* (2003; 2005). They studied four kinds of biomass (bagasse, pine sawdust, peanut shell, rice husk) in a fluidized bed reactor and found that the temperature was a key parameter due to biomass pyrolysis in a fluidized bed reactor.

Lu *et al.* (2005; 2007) developed hydrogen production technology by using supercritical water. He and other researchers (Guo *et al.*, 2006; Yan *et al.*, 2006) mixed several kinds of biomass in sodium carboxymethylcellulose, which was gasified successfully at 650°C, 25 MPa in a tubular flow reactor with formation of hydrogen, carbon dioxide, carbon monoxide, methane and a small amount of ethane and ethylene.

Furthermore, the domestic garbage gasification was studied by Yuan *et al.* (2002). Chen *et al.* (2003a,b; 2005; 2006; 2008) made progress in cogasification of biomass and glycerin. They studied four kinds of biomass in a two-stage reactor to produce hydrogen-rich gas, and investigated the effect of a catalytic bed on the pyrolysis behavior.

4.3.3 Biomass gasification gas as boiler fuel

4.3.3.1 The feasibility of biomass gasification gas as fuel

As China's energy situation becomes worse, the policy of national environmental protection has become stricter, and it is necessary to adapt to the actual situation of power generation technology to reduce operation and maintenance costs (Dong *et al.*, 2007). The safe operation of power generation enterprises has become more and more urgent. Using gas fuel especially some flammable industrial waste as a supplemental fuel cannot only help the power generation enterprises to reduce the production costs but also reduce the NO_x emissions of pollutants effectively.

Table 4.8. Components of biomass gasification gas and its low calorific value (Yuan *et al.*, 2005).

Varieties of raw materials	CO	H ₂	CH ₄	CO ₂	O ₂	N ₂	Net calorific value (under standard conditions) (kcal/kg)
Corn stalk	21.4	12.2	1.87	13.0	1.65	49.88	5328
Wheat straw	22.5	12.3	2.32	12.5	1.4	48.98	5033
Cotton stalk	22.7	11.5	1.92	11.6	1.5	50.78	3663
Rice husk	19.1	5.5	4.3	7.5	3.0	60.5	4594
New wood	20.0	12.0	2.0	11.0	0.2	54.5	4728
Leaves	15.1	15.1	0.8	13.1	0.6	54.6	3694
Sawdust	20.2	6.1	4.9	9.9	2.0	56.3	4544

Biomass is one of the earliest sources of energy, especially for the rural areas where biomass is the only accessible and affordable one. The waste from agriculture and industry can be used as raw material in biomass gasification for electric power generation. Gasification efficiency and system efficiency increase and tar content in fuel gas decreases when the gasification technology is put into operation. From the chemical point of view, the composition of biomass is a C-H compound. It exists in the conventional mineral sources of energy such as oil, coal and other similar sources (coal and oil are all biomass). Biomass generates organic compounds through photosynthesis by plants, including agriculture and forest waste (such as straw, straw, branches, etc.), firewood, crop residues from sugar industry, municipal organic waste, energy crops and animal waste. Their characteristics and utilization patterns have been very similar to those of fossils. Some biomass gas main compositions and low calorific values have been listed in Table 4.8.

China is rich in biomass resources, and except for firewood and livestock feed, most of them are burnt directly and with low utilization rate. Therefore, it is important to change the situation and to increase the energy utilization efficiency, which would promote the national economic development and environmental protection. Biomass energy utilization started in China late, but the development of boiler capacity has been very fast. More and more medium and large cities have formulated a corresponding demand. Regulations and restrictions on the use of fuel gas boilers, such as in Beijing, Shanghai, Xi'an, where construction of new coal-fired boiler room plant is no longer approved. After 10 years of development, from the pure laboratory research to pilot scale, biomass gasification has been successfully used in production practice. The Thermal Engineering Department of Harbin Institute of Technology has developed fluidized bed combustion technology for biomass energy utilization and has resulted in manufacturing of domestic combustion boilers, such as a 12.5 t/h bagasse fluidized bed boiler, a 4 t/h rice husk fluidized bed boiler, and a 10 t/h wood and sawdust fluidized bed boiler. The efficiencies are very high, up to 99%.

4.3.3.2 The superiority of biomass gasification gas as fuel

Biomass gasification gas is a good fuel. The benefits are summarized below:

- Low boiler equipment investment:
 - (i) There exists no heating side pollution, slag or wear problem. Compared with a coal boiler of equal capacity, a gas boiler is a compact structure, small size and lightweight, truly reducing the equipment investment.
 - (ii) It does not need soot blowers, dust, slag discharge equipment or fuel drying machines etc., thus, the systematic attached device is greatly simplified.
 - (iii) Since fuel storage is unnecessary, it can save transportation costs, and labor (Cao *et al.*, 2009).

- Low heating cost:
 - (i) It has strong adaptability in gas boiler heating load. Within the system, its adjustment is flexible and its gas measurement is simple and accurate, making it easy to adjust the gas supply.
 - (ii) With less accessory equipment, starting quickly and no fuel preparation system, it can reduce all kinds of consumption of preparation work, and electricity use is less than a coal boiler.
 - (iii) There are few particulate impurities in the gas, and the boiler will not be exposed to heating corrosion of high or low temperature. There exists no slagging problem. The boiler's continuous running cycle is long.
- Low equipment maintenance cost:
 - (i) The equipment of a gas boiler combustion system is simple, so there are less maintenance projects and lower maintenance cost.
 - (ii) Because there is no slagging and high temperature corrosion due to low operating temperature, heating pipes and air preheating element do not need to be replaced so frequently. With the rapid development of the gas industry, gas boilers and the extensive application of technology, accident-hidden danger are gradually reduced, and various protective measures are increasingly being perfected, which ensures the reliable operation of the gas boiler. Gas fired boilers in China are a new and booming industry, and has shown very broad prospects for development.

4.3.4 Biomass gasification gas used for drying

Combustible components of biomass gases mainly contain hydrogen, carbon monoxide and methane. They could be used for combustion and providing heat for power plant or for driving pyrolysis. Biomass gases can also be used for drying instead of flue gas (Yuan *et al.*, 2005). Thus, it is a convenient method for self-sufficiency. When the biomass gases can be used for drying agriculture and forestry products, it does not rigidly require the purity of exhaust gases after combustion. With air, the gases can be burned in all kinds of fireboxes continually and the equipment does not require cleaning and transportation long distance, and simply gives a short payback time. Compared to burning directly for heat, the efficiency is higher and it is valuable for small-scale companies and private business. Besides, biomass gasification gas can be used for drying of wood, grain, tobacco and tea directly at the same time.

4.3.5 Biomass gasification power generation

In recent years, biomass power generation technology research has progressed significantly in China. Experts predict that it will be mature in 2010 to 2020. The development direction of biomass power generation is combining cycle power generation (BIGCC) with advanced gas turbine power generation.

Biomass gasification power generation needs the following components: combustible gas is formed in a gasifier; the gas is purified and then burned in an internal combustion engine or combusted in a gas turbine to drive the generator to generate power. China has a good biomass gasification foundation, in the early nineteenth century; with charcoal gasification furnace gas, many cities in China used gas as a fuel for cars and other vehicles. In the energy shortage in the 1950s, China developed technology for rural irrigation and drainage machinery to provide power through firewood gasification furnaces, which has formed a series of product prototypes. Biomass gasification technology in the 1980s had more rapid development. In 1981 the first rice husk gasification power generation device was designed by Jiangsu Provincial Grain Bureau and a machine factory. This resulted in a 160 kW, downdraft gasifier with a Diesel Engine in Jiangsu. Later it was developed into a series of low heat value gas generators of 60, 160 and 200 kW.

The Tenth Five Year's Research Project of China is '160 kW fluidized bed biomass gasification generator technology industrialization research', and a demonstration unit was built in grain

processing factories in Anhui Lianhe Rice Industry Co., Ltd. Using straw, such as wheat straw and soft rice shell etc. as raw materials, with gas calorific value changing from 5200 kJ/m^3 to 5800 kJ/m^3 , with tar content was less than 20 mg/m^3 , the unit has already been put into operation and gained obvious economic benefits. In Anhui Lianhe Rice Industry Co., Ltd, a set of 400 kW biomass gasification generators were established. Since then, more and more biomass gasification generators have been built in China.

In the 20th century, the Academy of Sciences Guangzhou Energy Institute has studied the circulating fluidized bed of biomass gasification power generation technology. They had a lot of achievements and experience in development and commercialization. In 1991, the first circulating fluidized bed gasification device with diameter of 400 mm, height of 4 m, and feeding quantity 200–300 kg/h has been successfully developed by the Chinese Academy of Sciences Guangzhou Institute of Energy Development in Zhanjiang City. By making use of the wood powder waste, factory products convert into fuel gas as the fuel of boilers, and coal co-firing, each year replacing more than 3000 tonnes of coal. It obtained apparent social benefit and economic benefit. In 1998, the first circulating fluidized bed gasification device and internal combustion engine generator set, 1000 kW power rice husk gasification and power generation units in Fujian run successfully. Subsequently, in Hainan, a 1000 kW biomass demonstration power plant has run successfully for more than 3 years, and has promoted the foundation of more than 20 sets.

Below are some case studies of biomass power plant projects in China.

Case 1

A demonstration construction project of $2 \times 12 \text{ MW}$ biomass power plant in QuYang city of Shanxi Province, is a renewable energy project through combusting straw directly in the boiler generation. It is an effective way to implement the law of the People's Republic on renewable energy and the law of the People's Republic on saving energy, which is in accordance with the renewable energy management regulations and other related policies. Implementation of the project sets an example for effective utilization of renewable resources and the development of biomass power plant in the city and province.

Crop stalks (CSS) is a rich, clean, renewable and sustainable energy. Its development and utilization can not only reduce the sulfur dioxide emissions, solve the energy related problems of environmental pollution, and promote sustainable economic and social development, but also improve the coal-dominant energy structure and layout gradually in the province. The implementation of $2 \times 12 \text{ MW}$ biomass power plant demonstration project in QuYang city of Shanxi province, provide electricity safeguard for local power for local enterprise development, realize the economic and reasonable utilization of local abandoned straw, increase the farmers' income and improve the planting industry benefit; increase the fiscal revenue and local employment opportunities, and promote the development of the local economy. Using waste heat for central heating could save energy consumption, reduce environmental pollution and improve the quality of the urban life in many aspects.

With mature technologies, the demonstration project biomass power plant in QuYang city of Shanxi province has reliable economic benefit and significant social, ecological and environmental benefits. The scale of the project is $2 \times 12 \text{ MW}$, matching $2 \times 75 \text{ t/h}$ biomass (straw) circulating fluidized bed boiler. The total investment is 181.29 million Yuan; static investment is 172.38 million Yuan. With an annual consumption of 180,000 tonnes, the annual power generation is about $150 \times 10^6 \text{ kWh/y}$ at full load operation. With a price of 0.51651 Yuan/kWh (including taxes), the annual income is 78.96 million Yuan, while with a price of 0.44188 Yuan/kWh (not including tax), the annual income is 67.55 million Yuan. As a by-product, the annual output of chemical fertilizer is 9000 tonnes, increasing a value of 4.5 million Yuan. Using waste heat can create considerable income.

Using straw can solve three problems: energy shortage, environment protection, and addition to farmers' incomes. If 180,000 tonnes of straw are burnt in a year, it can save about 90,000 tonnes of standard coal, reduce sulfur dioxide emissions by 900 tonnes, smoke and dust emissions by

600 tonnes. If the price of straw is 60 Yuan per tonne, the project increases local farmers' income by more than 1000 Yuan per year.

Case 2

In Lishui city of Zhejiang province, an effective utilization of biomass gasification power of 10 MW has been built. Lishui city has a bamboo forest area of 1333.4 million m², occupying 15.6% of the area in Zhejiang province, which is a good resource base for developing biomass power. In this project, the produced gas is directly used in a gas engine for generating power. The single-machine capacity of the electric generator is 1000 kW and the project has a total of 10 units. As a by-product, the carbon product is 80 tonnes, the bamboo vinegar fluid product is 27 tonnes, and the wood tar product is 8 tonnes every day.

This project has a 10 MW generator production with a recovery bamboo charcoal and a bamboo vinegar fluid device. Its main components are raw material field, conveying system, bunker, drying, biomass gasifier, gas cooling and purification device, vinegar recycling equipment, carbon powder collection devices, gas generating sets, condensed water device and pipelines connecting the workshop etc.

The project's total investment is 110 million Yuan, of which the main equipment cost is 50 million Yuan, the cost of the carbon processing equipment is 2 million Yuan, the cost of electric Internet system is 10 million Yuan, the cost of land and building construction is 20 million Yuan, the technological cost is 7.5 million Yuan, the cost of the earlier stage is 5.5 million Yuan, the current fund is 15 million Yuan. After operating, the project income is 133.728 million Yuan, after tax is 18.2216 million Yuan.

Case 3

The project of biomass gasification power in Qing Yuan city of Zhejiang province, with an investment of 110 million Yuan, is one of the first biomass gasification power projects of the east China area, which is invested in by the China Forest Energy Corporation.

The poly-generation technology, using the principle of carbon, gas, liquid and hot water are produced during the biomass processing simultaneously. The combustible gas is injected into the generator power, and hot water will be used for heating, bamboo vinegar and bamboo charcoal are collected respectively for comprehensive utilization. This biomass gasification power generation technology is realizing straw and forest tree remains high efficiency and high added value using, which is in international leading level.

The biomass gasification power project consumes remains of bamboo processing and logging 80,000 tonnes to 100,000 tonnes, generating 72 million kWh power per year, producing 24,000 tonnes of bamboo charcoal, 8000 tonnes of bamboo vinegar fluid, and providing 3000 jobs, achieving an output of more than 130 million Yuan/year.

4.3.6 Biomass gasification for gas supply

According to the agricultural biomass energy industry development planning for 2007 to 2015 of China's Agriculture Ministry, 1000 straw gasification gas supply stations, with an annual capacity of 365 million cubic meters of gas from straw had been built by 2010, to solve the basic energy demands and changing the way China's countryside is used; 2000 straw gasification gas supply stations will be built by 2015, with an annual capacity of 730 million cubic meters of gas from straw.

In China, the institute of energy in Shandong province is the representative, whose rural straw gas centralized supply system gained major popularization and application. About 300 gas supply projects were built and a total investment of one hundred million Yuan was carried out. China has dozens of companies engaged in producing and marketing of rural straw gas centralized supply devices. Various types of straw were supplied as the main raw material in the straw gasification

technology. Thermal energy was supplied for cooking gas or drying food by central supply gas system. Farmers, especially the richest in well-off localities, eager to use clean energy, have changed the healthy and clean appearance of their villages. Because of straw gasification, farmers burn gas instead of wood, which met the demand of the farmers to improve the quality of life, and gained farmers' welcome and love.

There exist some problems in the straw gasification application for gas supply process. First of all, the gas centralized supply system of rural straw applied in China is the production of low calorific value biomass fuel gas with air medium. The flammable gas ingredient is CO, whose content is more than the regulations of the state civil gas standards. Farmer's culture, science and technology quality is low, especially in China, they have a big hidden danger of security with cooking gas. Secondly, the waste gas, produced by burning low value gas, would pollute the environment. In addition, the biggest problem of the Chinese straw gasification units in operation is the removal and processing of the tar. Therefore, the pipeline is easily blocked during the process because of tar precipitation, which is too little to recycle and be reused. If it is not removed, the environment will be polluted. Tar cracking is an effective method to solve the problem of pollution by tar, as showed in China's new energy nets. The problem of waste water containing tar could be solved if the quantity of tar is decreased greatly. It is hard to make the tar become cracked completely with the present technology, and water washing is needed to some degree. So wastewater treatment and recycling is necessary.

4.3.7 Hydrogen production from biomass gasification

As a flexible energy carrier that can be produced from a variety of resources and with comprehensive uses, hydrogen is one of the most promising substitutes for fossil fuels. It is certain that renewable-based hydrogen will be quite important in the future, especially hydrogen from biomass which has a series of unique merits. Technologies of hydrogen production from biomass mainly contains two kinds of processes. One is the thermo-chemical route, including biomass/waste gasification, biomass pyrolysis, hydrogen from biomass derived methane/methanol/ethanol; the other is the biological route, including direct bio-photolysis, indirect bio-photolysis photo fermentation, hydrogen synthesis *via* the water gas shift reaction of photo-heterotrophic bacteria, dark fermentation and microbial fuel cells, etc (Chen *et al.*, 2006).

The catalytic hydrogen production technology route of Lü *et al.* (2004b) research is: CFB and fixed bed are used as reactors, and the catalyst is a mixture of dolomite and nickel-based powder. Dolomite is used as bed material and catalyst, and Ni-based catalyst is placed at outlet of the CFB. The results show that the volume content of hydrogen is more than 50%, and content of CO₂ is lower than 1%, gas yield could reach 3.31 Nm³/kg, productivity of hydrogen is 130.28 g/kg biomass.

In the State Key Laboratory of multiphase flow in power engineering of Xi'an Jiao Tong University, Yan *et al.* (2005) have done much work on supercritical water gasification and solar energy catalyzed biomass for hydrogen production. In their study, biomass was used as raw material and an Ni-based alloy tube was taken as reactor. Supercritical water-gasification processed at 650°C under a pressure of 25 MPa. Experimental results indicated that volume content of hydrogen is 41.28%, and the small size of biomass particles favor of the production of hydrogen. Besides, the wall of the reactor could enhance the production of hydrogen (Guo *et al.*, 2005).

The Institute of Coal Chemistry, Chinese Academy of Science has studied the CFB conversion of biomass and supercritical water conversion for hydrogen production. The feasibility of total processing of biomass and coal was investigated in the CFB. Besides, hydrogen production from sawdust was processed under supercritical pressure at 773–923 K, and batch-type supercritical water reactor was used as reaction chamber. It was found that the molar ratio of calcium and carbon has a great influence on the conversion of sawdust. Gas conversion of carbon and the gas yield of hydrogen is doubled when the molar ratio of calcium and carbon equals to 0.48. Besides, reaction temperature also has great impact on gas yield of hydrogen.

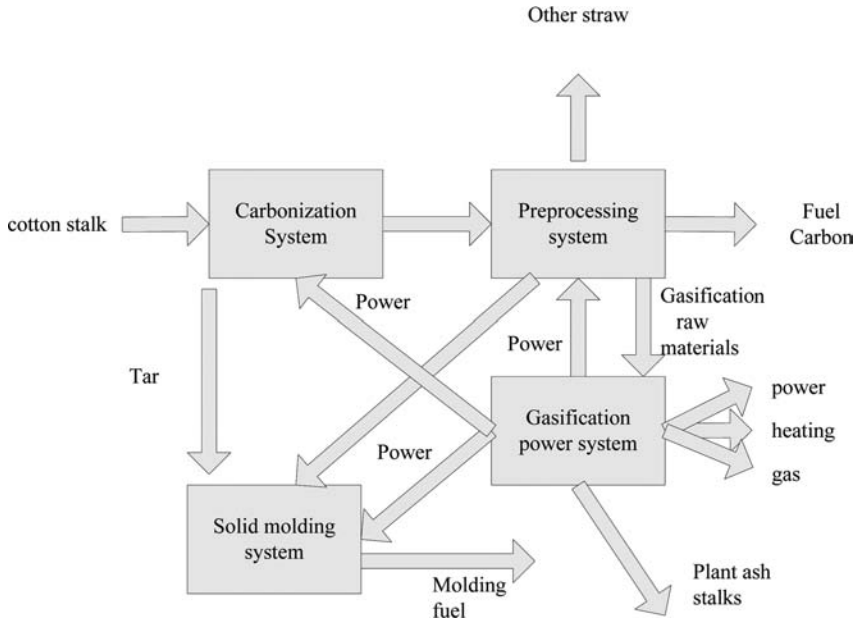


Figure 4.10. Polygeneration scheme of cotton stalk system.

The Institute for Thermal Power Engineering of Zhejiang University has developed steam-gas co-production of biomass and coal experiment and a mechanism study which aim at obtaining combustion gas. The synthetic gas was tested in a double CFB circulating system and the calorific value can reach 2800 kcal/Nm^3 , and conversion of fuel is 95%. Based on these results, biomass conversion for hydrogen production is under investigation at present, including the separation of CO_2 .

Tianjin University is famous for catalytic pyrolyzation of biomass for hydrogen-rich gas, and has proposed the technology route of fast pyrolysis-catalyst steam reforming. A two stage catalyzed gasification hydrogen production system, which includes CFB gasification reactor and fixed bed, was built. The impact of operation parameters, design parameters and catalyst type to the gas yield were investigated, and the results showed that the volume of hydrogen-rich gas can reach 50–65% (Chen *et al.*, 2003b).

4.3.8 Biomass gasification polygeneration scheme

In China Industrial Competitive Intelligence Research, Wuhan city circle is a base for grain, oil and cotton, which contains Wuhan, Huangshi, Ezhou, Xiaogan, Huanggang, Xianning, Xiantao, Tianmen, Qianjiang, where agriculture is developed and arich source of biomass energy. According to the essential characteristic of village biomass and its distribution, combining the status of biomass utilization, two important comprehensive utilization projects of two main biomass sources are put forward, which are the polygeneration scheme of cotton stalk system (Fig. 4.10 and Fig. 4.11) and the rice husk system (Fig. 4.12).

It is found that the straw enrichment area can be classified into two categories. In the first category, there are cotton stalks in the field, and other resources are classified according to the production of straw or wheat-straw. In the second category, there are no cotton stalks in the fields and they have plenty of straw. The two types of drawing the all-round systems are shown in Figure 4.10 and 4.11, respectively.

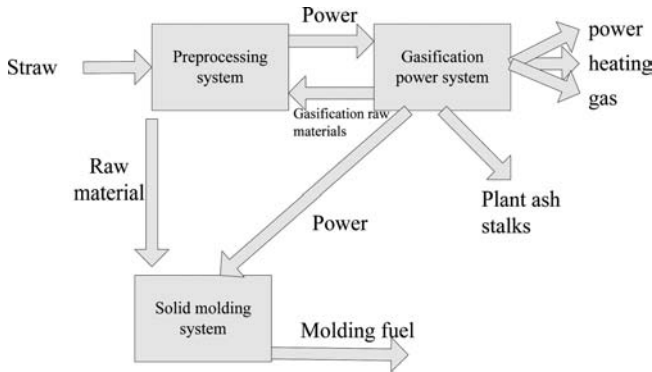


Figure 4.11. Polygeneration scheme of straw system.

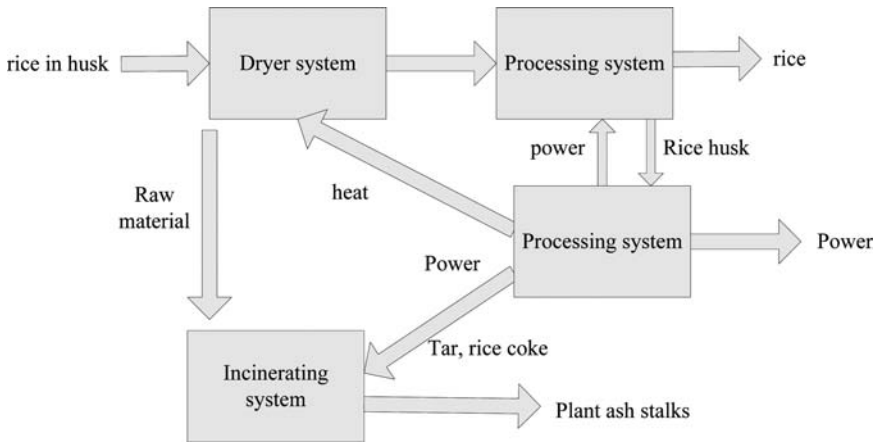


Figure 4.12. Polygeneration scheme of rice husk system.

The utilization of straw in the polygeneration system is effective. Without external basic energy, subsystems are coordinated to eliminate secondary pollutants, and overcome the problem that single technology of using biomass suffers from with poor economic returns, and by generation of secondary pollution.

As is shown in Figure 4.12, the rice husk poly-generation system connect the rice processing and rice husk utilization, making full use of the energy in the rice husk, and solving pollution problem of secondary ash accumulation. This system consists of some subsystems, such as rice husk gasification power generation, rice processing, rice drying, and rice coke burning systems. The rice husk poly-generation systems decreases the cost of producing rice because it needs to consume not any external energy. At the same time, the system supplies power for its own operation, while transferring the dump power to resident's homes. The ash can be used for steel works and white carbon black production. It shows a great potential economic value.

4.3.9 Policy-oriented biomass gasification in China

In order to ensure the steady development of Biomass gasification industry, the Chinese government issued a series of laws, regulations and policy measures to actively promote the development of biomass gasification technology.

4.3.9.1 *Guide public awareness*

China promulgated the “New Energy Law”, “renewable energy industry catalogue” in 2005, issued the “Renewable Energy Law”, “renewable energy for the generation of regulations”, “renewable energy prices and cost-sharing management pilot scheme” and “Renewable energy development special fund Interim Measures” in 2006. A sound legal framework has been established through a series of laws and regulations. Then the management of various aspects, such as energy development, investment, production and consumption can be conducted under the protection of the law. The “long-term renewable energy development plan” released in November 2007 developed a specific strategy and goals for sustainable energy development, and clearly proposed taking advantage of biogas and waste gasification technology to improve the proportion of gas used in rural areas. What’s more, it also identified the biomass gasification technology as an important measure to solve the problem of rural waste and industrial organic waste. Since then, the biomass gasification technology has developed into a new stage.

4.3.9.2 *Government investment in R&D of key technologies*

The key technology of biomass gasification research and development is usually based on the government’s advanced investment, then the industry world and business world would follow-up and quickly realize the technology industrialization and commercialization. The Chinese government realized the issue “total risk, share results” by strengthening the public-sector research institutions and private sector cooperation and effectively led the development of the biomass gasification technology initiative. The Chinese Academy of Sciences Guangzhou Institute of Energy carried on the MW level biomass gasification power generation system research in the Ninth Five-Year Plan period, aiming at developing medium-size biomass gasification power generation technology for Chinese market demand and resource characteristics. Its power demonstration system was completed in October 1998 and put into use.

“Agricultural Biomass Industry Development Plan” introduced in 2007 submitted the recent focus on gasification technology: first, continue to expand the scope of straw gasification demonstration and perfect the biogas technology of straw production. The second is to strengthen and standardize the operation and management of straw gasification stations. The third is to solve the problem of high tar content in the straw gasification fuel and improve the stability of the system. The planning also proposed that China would build 1000 straw gasification gas stations till 2015, and annual output gas straw would reach 365 million cubic meters.

4.3.9.3 *Fiscal incentives and market regulation measures*

The Chinese government follows the “market-based” principle, and puts “market measures” as a main tool to encourage and guide the development of biomass gasification technology. A series of fiscal incentives, such as financial assistance, tax breaks, investment subsidies, interest-free, subsidized loans etc, have also been developed and implemented, to encourage businesses to use biomass gasification technology. In addition, the Chinese Ministry of Finance, National Development and Reform Commission jointly issued “On the development of bio-energy and bio-chemical and taxation policies to support the implementation of views” in 2006 to propose tax incentives: “the state will give tax incentives to some bio-energy and bio-chemical companies who really need support to enhance the competitiveness of enterprises.” Appropriate guidance from public policy can make some companies, whose motivation is pursuing the most interest, put the biomass gasification technology as their “rational choice”.

4.4 CONCLUSIONS

4.4.1 *Co-combustion*

The development of renewable energy is supported strongly by the Chinese government. Biomass co-firing technology is one of the key technologies supported. But it still has not resulted in

corresponding economic incentive policy for biomass co-firing. There are a large number of small and medium-sized coal fired generators forced out and closed, which instead could be combined with abundant biomass energy resources. Concerning biomass co-firing technology, there are certain project barriers: less project experience, lack of resources, lack of support system and technical system support, uncertain project factors, more difficult financing. Biomass co-firing projects need more support and motivation.

4.4.2 Gasification

Gasification is a versatile thermo-chemical conversion process which produces a gas mixture of CH_4 , CO , and H_2 , the proportions of which are determined by the use of air, oxygen or steam as the gasification medium. Biomass gasification has broad prospects in China. Biomass gasification technology will make great progress, and the heating value of gas produced will be higher with the advanced technology. Biomass gasification now used in poly-generation becomes more and more popular, and can give energy at a maximum level. Using the technology, energy utilization efficiency could be increased.

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CHAPTER 5

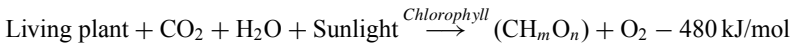
Biomass combustion and chemical looping for carbon capture and storage

Umberto Desideri & Francesco Fantozzi

5.1 FEEDSTOCK PROPERTIES

5.1.1 Biomass and biofuels definition and classification

According to a general definition biomass may be considered as animal and plant resources and the wastes deriving from their treatment, which could be used, directly or after a pretreatment as a source of energy. It is therefore a resource directly or indirectly resulting from the photosynthesis process, represented by the following equation (Klass, 1998):



For every mole of CO_2 absorbed 1 mole of oxygen is released. Zhu *et al.* (2008) have shown that the maximum conversion efficiency of solar energy to biomass is 4.6% for C3 photosynthesis at 30°C and today's 380 ppm atmospheric concentration of CO_2 , while C4 plants have an efficiency of about 6%. Losses are distributed thus: loss by reflectance of photo-synthetically active light (4.9% for example); loss in rapid relaxation of higher excited states of chlorophyll (6.6% for example); loss between the reaction center and carbohydrate synthesis (24.6% for C3 plants and 28.7% for C4 plants, for example); loss due to photorespiration (around 6.1% for C3 plants and 0% for C4 plants); loss due to respiration (1.9% for C3 plants and 2.5% for C4 plants). Figure 5.1 shows the minimum energy losses calculated for 1000 kJ of incident solar radiation.

When considering its use as a fuel the interest is focused on combustible materials resulting directly from silviculture, agriculture, aquaculture, farming, and the related transformation

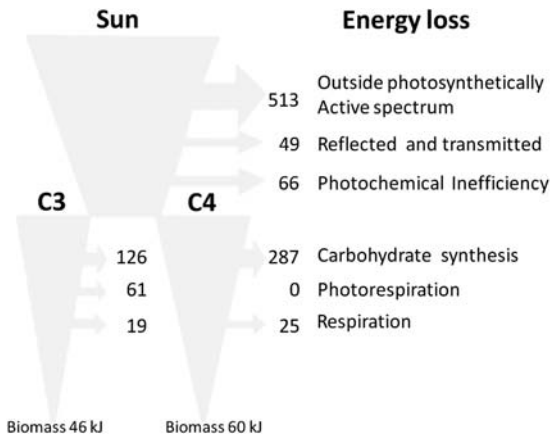


Figure 5.1. Minimum energy losses calculated for 1000 kJ of incident solar radiation (Zhu *et al.*, 2008)

industries (e.g. wood and food industries), or indirectly through their preprocessing to obtain better performing fuels (biofuels) with respect to the initial state (Williams *et al.*, 2012; Tillman, 1991).

Different classifications of biomass are possible according to their origin, characteristics or use; however from an energy point of view its importance is linked to its potential to yield a competitive biofuel that may replace a fossil fuel, therefore a useful classification should consider the environmental and economic effectiveness of its energy conversion. From this point view, since the primal transformation is photosynthesis, biomass energy content is somehow deriving from low density solar energy and, most important, biomass is a geographically distributed resource scattered on a wide area, as it is solar radiation.

This turns into a low energy content per volume product which needs to be produced, collected and transported hence its economic and environmental competitiveness is strongly dependent on the overall balance resulting from the different phases (supply chain).

According to this view, a possible general classification of biomasses (and/or biofuels) could consider different categories as a function of how many phases (and their resulting economic and environmental burden) are necessary to obtain available biomass as a fuel or as a feedstock to obtain a biofuel. Three categories therefore can be identified as follows.

(a) *Energy crops*: They are dedicated crops specifically cultivated for energy purposes. This is the worst performing category since the economic-environmental burden of the production phase and of the gathering-transportation phase is totally allocated to the final product. However these biomasses may provide a useful (sometimes unique) solution for agriculture revival in depressed or contaminated areas.

They can be divided into no-food crops and food crops depending on their possible competition as a raw material for the food industry.

Among the no-food crops short rotation crops such as woody (poplar, black locust, eucalyptus, etc.) and herbaceous crops (miscanthus, giant reed, kenaf, sorghum, etc.) are utilized for direct combustion or for second-generation bioethanol production as a source of cellulose. There is also an increasing interest in algae for biomass and oil production.

Among the food crops the main interest is in high sugar or starch content crops, for bioethanol production (corn, sugarcane, sugar beet, etc.) or oily fruits for oil extraction to use directly as a fuel or for the production of biodiesel (sunflower, rapeseed, palm and soybean).

(b) *Residual biomasses*: They are residues of agricultural crops and forestry maintenance. These biomasses do not comprehend the economic-environmental burden of the production phase, since its cost is allocated on the primary product (vegetables or wood) while still comprehending the burden of the gathering-transportation phase. The gathering in particular may still be an issue if the harvesting of the primary product does not consider a proper handling of the byproduct.

Residual biomasses comprise:

- Agricultural residues (pruning, straw, corn/sunflower/tobacco stovers, etc.);
- Forestry residues (pruning, branches, tops, sawdust etc.);
- Urban green residues (pruning, branches, sawdust, etc.).

(c) *Agro industrial and farming residues*: They represent the byproducts of the food, wood, pulp and paper, and animal farming industry. This is the best performing category since the economic-environmental burden of the production phase and of the gathering-transportation phase is totally allocated to the final product, leaving a cost free biomass available in a single site. Moreover these residues are often to be disposed of therefore their energy conversion could also represent an avoided cost.

They can be divided into:

- agro-food industry residues (oil industry (pomace), wine industry (vinasse), dairy industry (whey), meat industry (meat and bone meal, tallow, etc.), fruit industry (skins, shells, stones, etc.) pulp and paper industry (residues), cereals industry (rice and grain husk, frying oils, etc.);
- animal farming residues (swine and cow manure, poultry litter, feathers, etc.);

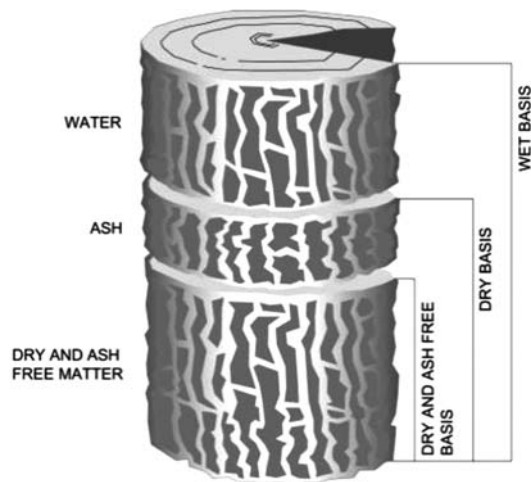


Figure 5.2. Reference base for solid fuel main components.

- urban and industrial residues (organic fraction of MSW (Municipal Solid Waste), sewage sludge, pallets and packaging residues, paper and cardboard, etc.).

With some notable exceptions (waste frying oils, cereal husks, paper and cardboard, etc.) most of agro-industrial residues have a very high humidity content which is not suitable for direct combustion application, while biological treatment such as anaerobic digestion is preferable.

A general classification of biomass can be found in UNI-EN 14961-1 “Solid biofuels: Fuel specifications and classes – Part 1: General requirements (EN 14961-1, 2010)”.

5.1.2 Biomass composition and analysis

To evaluate which conversion process is more suitable for different biomasses, a preliminary characterization is necessary to analyze their chemical, physical and energetic properties.

Biomass is composed of water, ashes and dry matter without ashes and only the latter component is interesting for energy conversion yielding a calorific value. Ashes and water decrease the commercial value of biomass because:

- they decrease the bulk energy content of biomass;
- moisture absorbs energy for evaporation;
- ashes have to be disposed of;
- light ashes are transported by flue gases and contribute to PM (particulate matter) emissions;
- low melting point ashes foul heat exchangers.

Given the presence of these three different main components, the measurable quantities contained in a biomass can be expressed (Fig. 5.2):

- On a wet basis (wb) or as received basis (ar): with reference to the whole quantity therefore considering the percentage with respect to the total of ash, water and ash-free matter. Referring to wet basis is useful when the effective quantity of a certain measure (for example energy content) per mass (or volume) unit is required; it is a measure directly linked to the economic price of biomass and to management costs (transport, storage etc.). However, it is not a characteristic and fixed measurement since the humidity may vary considerably in time and space for a specified biomass.

Table 5.1. Selected biomass characteristics. *VM*: volatile matter, *HHV*: higher heating value, *LHV*: lower heating value (Mancosu, 2011)

Biomass	Moisture [%] wb	VM [%]	Ashes [%]	C [%]	H [%]	N [%]	HHV [MJ/kg _{db}]	LHV [MJ/kg _{db}]	Bulk density [kg/m ³]
Oak wood	6.2	86.0	0.9	49.7	6.5	0.2	20.4	18.9	750
Pine wood	9.5	89.3	0.7	51.3	6.1	0.2	19.2	—	440–560
Pine bark	—	—	1.8	46.9	5.3	—	—	—	—
Pellet	10.0	85.6	0.8	49.8	6.4	0.3	18.5	17.4	650
Sorghum	—	—	2.1	43.9	6.2	0.2	16.8	—	220–260
Salix wood	7.9	85.7	1.9	49.1	6.2	0.3	18.8	—	300–400
Poplar wood	8.6	80.3	1.3	49.7	6.5	0.2	19.6	19.3	420
Fire wood	7.7	77.0	5.8	48.6	6.5	0.2	18.9	—	700–800
Birch wood	7.4	80.9	2.6	48.3	8.3	0.1	19.3	—	600
Vine pruning	45.0	86.0	2.3	46.5	6.4	0.4	18.6	17.1	790–900
Olive tree pruning	40.0	86.0	3.9	49.3	5.5	0.6	18.5	17.4	800–900
Sawdust	11.6	81.5	0.8	49.5	6.8	0.4	19.7	—	100
Bamboo	8.5	76.5	0.8	50.6	5.3	0.2	19.3	—	200–250
Wood chips	9.3	88.0	1.0	50.0	5.8	0.3	19.3	—	150
Giant reed	40.0	—	8.5	45.5	5.7	0.2	18.0	17.5	180–200
Black locust	30.0	85.7	3.6	50.7	5.7	0.5	19.7	18.5	625
Straw	8.7	72.3	14.9	43.0	6.3	0.8	16.0	14.9	100–180
Wheat	6.4	75.0	8.0	43.0	10.85	0.3	16.0	—	—
Rice husk	—	69.3	19.0	36.7	5.0	0.9	14.5	13.9	75
Sugarcane	—	85.2	2.2	52.5	6.8	0.5	18.9	—	130–150
Rapeseed	6.1	77.6	3.8	42.4	7.1	0.2	16.6	—	—
Stone fruit resid.	6.9	85.6	0.5	51.6	6.0	0.5	21.6	—	—
Almond shell	8.7	81.7	2.8	52.4	6.7	0.5	19.0	17.7	—
Hazelnut shell	9.3	71.0	7.9	42.8	5.15	0.6	15.7	—	—
Walnut shell	6.7	76.1	3.6	51.5	7.3	0.7	—	—	—
Tomato	7.0	86.1	3.8	52.3	7.6	3.4	—	—	—
Olive husk	8.3	78.4	6.4	49.6	5.5	1.4	20.9	19.1	—
Bagasse	—	77.7	2.1	51.5	6.0	1.0	18.2	—	—

- On a dry basis (db): with reference to the whole quantity subtracted of water content, therefore considering the percentage with respect to the total of ash and ash-free matter. Referring to the dry basis is useful because the measurement does not vary in time however it might lead to over- or under-estimation of some properties (e.g. low heating value) if a proper humidity content is not considered when extrapolating data to a real context.
- On dry and ash-free basis (dafb): with reference to the whole quantity subtracted of water and ash content, therefore considering the percentage with respect to the ash-free matter. Referring to the dry and ash-free basis considers only the mass that yields energy content and may be useful when utilizing literature data referring to the main constituents (e.g. cellulose, hemicellulose and lignin).

A typical characterization of woody and herbaceous biomasses is reported in Table 5.1 (Mancosu, 2011).

5.1.3 Biomass analysis

To characterize biomass as a fuel usually proximate and ultimate analysis are used (Miller and Tillman, 2008). Proximate analysis is defined as “the determination, by prescribed methods, of moisture, volatile matter, fixed carbon (by difference), and ash” (ASTM D 3172-07).

Ultimate analysis is defined as “the determination of the elemental composition of the organic portion of carbonaceous materials, as well as the total ash and moisture” (Miller and Tillman, 2008; ASTM D 5373-02; Milne *et al.*, 1990).

5.1.3.1 Moisture content (EN 14774-2, 2009)

It represents the quantity of water inside the sample, expressed as a percentage of the weight of the material. The moisture content (MC_{wb}) referred to wet basis is expressed as the ratio between water content and the weight of biomass (obtained as the sum of the components: water, ashes, dry and ash free matter):

$$MC_{wb} = 100 \frac{m_{H_2O}}{m_b} = 100 \frac{m_{H_2O}}{m_{daf} + m_{H_2O} + m_{ash}} \quad (5.1)$$

Moisture on dry basis (MC_{db}) is expressed as the ratio between the weight of water contained in biomass and the weight of ashes plus the weight of dry matter without ashes:

$$MC_{db} = 100 \frac{m_{H_2O}}{m_b - m_{H_2O}} = 100 \frac{m_{H_2O}}{m_{daf} + m_{ash}} \quad (5.2)$$

Moisture on dry and ash-free basis (MC_{dafb}) is expressed as the ratio between the weight of the water contained in biomass and the weight of dry matter without ashes:

$$MC_{dafb} = 100 \frac{m_{H_2O}}{m_b - m_{H_2O} - m_{ash}} = 100 \frac{m_{H_2O}}{m_{dafb}} \quad (5.3)$$

Moisture on wet basis is calculated as a variation in mass between the sample as received and the oven dried sample at a temperature equal to $105 \pm 2^\circ\text{C}$ till the weight variation becomes negligible.

5.1.3.2 Ash content (EN 14775, 2009)

Ashes are defined as the residual mass obtained after combustion in air, under controlled conditions of time and temperature; in a similar way to moisture, ash content can be calculated on wet basis, on dry basis and on dry and ash-free basis. Usually the value referred to dry basis is used. Ashes obtained from wood combustion are composed mainly of: silicon, calcium, potassium, phosphorus, manganese, iron, zinc, sodium, boron, in the form of oxides, silicates and nitrates. For their composition ashes are generally alkaline, with a pH around 12; the chemical composition may also vary depending on the combustion temperature.

Table 5.2 shows a typical ash composition for different biomasses together with their melting point which constitutes a main issue to tackle during combustion. Some biomasses show ashes with a particularly low melting temperature which may adhere to surfaces inside the combustion chamber and also cause heat-exchanger fouling. To avoid ash melting, a limit on the combustion temperature should be considered hence the resulting power cycle efficiency and emission control may be affected.

5.1.3.3 Volatile matter (EN 15148, 2009)

This represents the part of biomass that is released during heating ($200\text{--}450^\circ\text{C}$) without oxygen (pyrolysis). Pyrolysis process also happens during biomass combustion, because oxygen does not reach the internal layers of the fuel with the same velocity with which heat does. For this reason while the external layer of biomass burns, the internal layer decomposes due to pyrolysis. During this process biomass decomposes in non-condensable gases (syngas), condensable gases (tars) and solid carbon (char): the first two products can be grouped under the category: volatile matter (VM) (EN 15148, 2009).

Table 5.2. Ash characteristics of selected biomasses.

		Ash composition [% wt, ash db]	Sintering temperature [°C]	Softening temperature [°C]	Hemisphere temperature [°C]	Melting temperature [°C]
Wood (spruce)	Si	4.0–11.0	1110–1340	1410–1640	1630 → 1700	>1700
	Ca	26.0–38.0				
	Mg	2.2–3.6				
	K	4.9–6.3				
	Na	0.3–0.5				
	P	0.8–1.9				
Bark (spruce)	Si	7.0–17.0	1250–1390	1320–1680	1340 → 1700	1410 → 1700
	Ca	24.0–36.0				
	Mg	2.4–5.6				
	K	5.0–9.9				
	Na	0.5–0.7				
	P	1.0–1.9				
Straw (winter wheat)	Si	16.0–30.0	800–860	860–900	1040–1130	1080–1120
	Ca	4.5–8.0				
	Mg	1.1–2.7				
	K	10.0–16.0				
	Na	0.2–1.0				
	P	0.2–6.7				
Cereals	Si	16.0–26.0	970–1010	1020	1120–1170	1180–1220
	Ca	3.0–7.0				
	Mg	1.2–2.6				
	K	11.0–18.0				
	Na	0.2–0.5				
	P	4.5–6.8				

(Nussbaumer, 1993; Lewandowsky, 1996; Obernberger *et al.*, 2000; Ruckebauer, 1996; Schmidt *et al.*, 1994; Obernberger *et al.*, 1996; Channiwala and Parikh, 2002).

The content of volatile matter is determined by heating the fuel in absence of oxygen and in strictly controlled conditions and it is calculated using the following relation:

$$VM = \left(\frac{m_1 - m_2}{m_1} \right) \times 100 \quad (5.4)$$

where:

VM = % of volatile matter in the air-dried sample [%]

m_1 = sample mass before heating [g]

m_2 = sample mass after heating [g].

Volatile matter as well can be expressed on a wet basis, dry basis or dry and ash-free basis. The volatile matter content is important because it determines the quantity of secondary combustion air to provide inside the combustion chamber; primary air being the one necessary to oxidize solid char.

5.1.3.4 Heating value (EN 14918, 2009)

This represents the heat released during the complete combustion of a sample, determined by burning it in a controlled environment; it is expressed as the energy content per mass unit (kJ/kg, MJ/kg) and can be referred to the wet basis, the dry basis or the dry and ash-free, basis. It can be divided into: higher heating value (HHV) and lower heating value (LHV), depending on whether

water obtained as a product of combustion is considered in liquid phase or vapor. The difference between HHV and LHV is therefore the latent heat of condensation of the steam present in the combustion products. It has to be noted however that the water content to be considered in exhaust gases, when calculating LHV from HHV is only the one derived by the oxidation of hydrogen present in the sample; steam coming from moisture in the sample is not considered in the LHV therefore HHV should be always corrected on a dry sample.

The relations that describe these quantities are:

Higher Heating Value (HHV):

$$HHV_{wb} = HHV_{dafb} \left(1 - \frac{AC_{wb}}{100} - \frac{MC_{wb}}{100} \right) [\text{kJ/kg}_{wb}] \quad (5.5)$$

$$HHV_{db} = HHV_{dafb} \left(1 - \frac{AC_{db}}{100} \right) [\text{kJ/kg}_{wb}] \quad (5.6)$$

Lower Heating Value (LHV):

$$LHV_{db} = LHV_{dafb} \left(1 - \frac{AC_{wb}}{100} - \frac{MC_{wb}}{100} \right) [\text{kJ/kg}_{wb}] \quad (5.7)$$

$$LHV_{db} = LHV_{dafb} \left(1 - \frac{AC_{db}}{100} \right) [\text{kJ/kg}_{wb}] \quad (5.8)$$

The HHV is measured in laboratory using a calorimeter. The LHV is obtained, knowing the hydrogen content of the sample (determined through elemental analysis with a CHN analyzer) through the following relation:

$$LHV_{db} = HHV_{db} - 206.0 H_{db} [\text{kJ/kg}_{wb}] \quad (5.9)$$

in which H_{db} is the content of hydrogen expressed in mass and referred to the dry basis. The heating value is a fundamental parameter that gives indications on the energetic potential of the biofuel. In fact the higher the heating value the higher is the energy yield per unit of mass obtained by the conversion process.

At operative level it is better to consider the heating value on dry basis, because it represents the real energy yield of the fuel. Moisture content lowers the energy content of biomass because the evaporation consumes energy that could be used for the thermo-chemical conversion processes.

The heating value can be calculated also through formulas derived from correlations, for example the Channiwala Parikh formula that correlates HHV with the elemental analysis (Demirbas, 2004):

$$HHV = 349.1 C + 1178.3 H + 100.5 S - 103.4 O - 15.1 N - 21.1 \text{ Ash} [\text{kJ/kg}] \quad (5.10)$$

Other attempts have been made to derive a heating value from proximate analysis (Parikh *et al.*, 2005).

5.1.3.5 Carbon, hydrogen and nitrogen content (EN 15104, 2011)

The concentration of the three elements in the biomass sample is measured through the ultimate analysis of the sample, that is the combustion of the same in controlled atmosphere and the successive analysis of flue gases. The three concentrations obtained are expressed in % dafb. The carbon/nitrogen ratio can be used as an indicator to identify the most suitable conversion technique for the biomass. When the C/N ratio is higher than 30, the thermochemical conversion process could be adopted, while when C/N is lower than 30, the most suitable conversion processes are biochemical processes.

5.1.3.6 Density (EN 15103, 2010)

This represents the weight of biomass per unit of volume and can be expressed on dry basis and on wet basis, indicating the value of moisture content. Another important parameter is the bulk density that expresses the volumes required for storage. Typical values of the bulk density range from 150–200 kg/m³ for straw and wood chips, to about 600–900 kg/m³ for wood. Table 5.1 shows typical values for bulk density of selected biomasses. Together with heating value the bulk density identifies the energy density of biomass, that is the energy available per unit of volume. This information is necessary to design the storage facilities and to evaluate transportation costs. In general the energetic density of biomass is about 1/10 that of fossil fuels.

5.1.3.7 Sulfur content analysis (EN 15289, 2011)

This represents the quantity of inorganic and organic sulfur contained in biomass. The measure is realized eliminating all the organic substances present in the fuel and operating the complete transformation of sulfur compounds in soluble sulfates, through calcination at elevated temperatures in oxidizing and basic environments. The content of sulfur in the fuel is responsible for the presence and quantity of sulfur oxides (and so acid gases of sulfur: sulfuric acid and hydrogen sulfide) in the emissions deriving from energy conversion processes.

5.1.3.8 Chlorine and fluorine content analysis (EN 15289, 2011)

This can be expressed as: total chlorine/fluorine, water soluble chlorine/fluorine and water insoluble chlorine/fluorine. Dealing with total chlorine/fluorine the sample is burned in an oxygen atmosphere transforming chlorine into chlorides and fluorine into fluorides and with the successive absorption in an alkaline solution. Chlorine and fluorine in solution are determined through potentiometric titration. Soluble chlorides/fluorides are measured by extracting a portion of the sample with water and then through potentiometric titration. Insoluble chlorine/fluorine is calculated subtracting the soluble components from the total. The eventual content of chlorine and fluorine in biomass is responsible for the emission of acid gases (HCl and HF) and also dioxins and furans.

5.1.3.9 Chemical analysis (EN 15297, 2011 and EN 15290, 2011)

Other trace elements in the fuel have to be analyzed: As, Cd, Co, Cr, Cu, Hg, Mo, Mn, Ni, Pb, Sb, Se, Sn, V, Zn, Al, Si, K, Na, Ca, Mg, Fe, P and Ti, using methodologies and instrumentations adequate for the specific element. The presence of these elements in the fuel influences the choice of the conversion process to be adopted. As an example Miles *et al.* (1996) showed that Ca and Mg increase the melting temperature of ashes, while K and Na decrease it; Si if combined with K and Na can form low-melting silicates.

The behavior of ashes and the technical standard used for the determination of ash melting behavior will be analyzed in a specific section.

5.1.3.10 Size (CEN/TS 15149-1:2006, CEN/TS 15149-2:2006, CEN/TS 15149-3:2006)

This parameter is essential for the optimization of the energy conversion process, because inadequate particle size can cause the following problems: clogging or system damage in conveying and transportation, bridging in storage and conveying systems, increasing resistance to air flow in aeration and drying, inhibition of particle spreading on fire beds, dust formation during transportation, combustion efficiency and emissions control. There are three methods available to determine biofuel size: oscillating screen, vibrating screen and rotating screen method; however, they all measure the quantity of biomass, which is sieved through screens of varying dimensions.

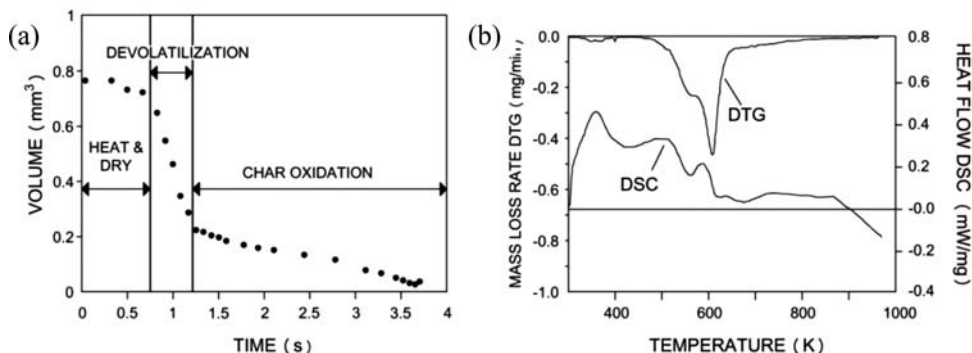
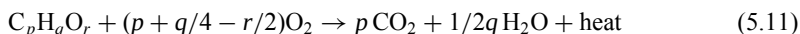


Figure 5.3. (a) Typical mass loss rate during the combustion of a biomass particle; (b) Differential Thermo Gravimetry (DTG) and Differential Scan Calorimetry (DSC) curves for wheat straw combustion.

5.2 COMBUSTION BASICS

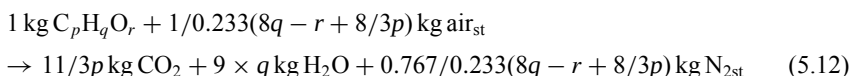
5.2.1 Introduction

Combustion can be defined as “an exothermic oxidation process occurring at a relatively high temperature” (Basu, 2001). A simplified stoichiometry of the reaction for a biomass of generic composition is the following (Tillman, 1991):



O_2 used as an oxidant is usually provided through combustion air therefore assuming a standard volume composition of air (79% N_2 and 21% O_2) so also $(3.76 \times n) N_2$ has to be considered, n being the number of moles of oxygen required to complete the combustion of the fuel.

Stoichiometric or ideal combustion for a biomass (with the following composition: p carbon mass fraction; q hydrogen mass fraction, r oxygen mass fraction) can therefore be simplified as:



The combustion of biomass can be described as the steps followed by the biofuel to undergo a complete oxidation. Four steps can be identified (Browne, 1958): drying and heating, solid particle pyrolysis, char oxidation and volatile oxidation (Fig. 5.3) (van Loo and Kopperjan, 2002; He *et al.*, 2006).

A biomass particle that enters a hot combustion chamber is rapidly heated from the outside to its internal core. Heat is transferred from the furnace to the particle outer layer through radiation-convection from flame and flue gases and conduction from the hot biomass bed while conductive heat transfer brings heat inside the particle. The temperature increases abruptly in the outer layer but slowly towards the core of the particle therefore humidity evaporation begins in the external layer and proceeds towards the inside with an evaporation front which is considered to happen conventionally when the layer reaches 105°C. Water evaporates and its expansion cracks the particles producing micro and meso-pores through which steam is ejected. The dried layers increase further their temperature, but cannot burn because oxygen does not reach the inner layers, eventually hemicellulose first and cellulose-lignin after start to decompose thermally. Long polymeric chains are cracked into smaller ones which vaporize or become permanent gases leaving the particles through the same paths followed by steam. This mixture of permanent gases

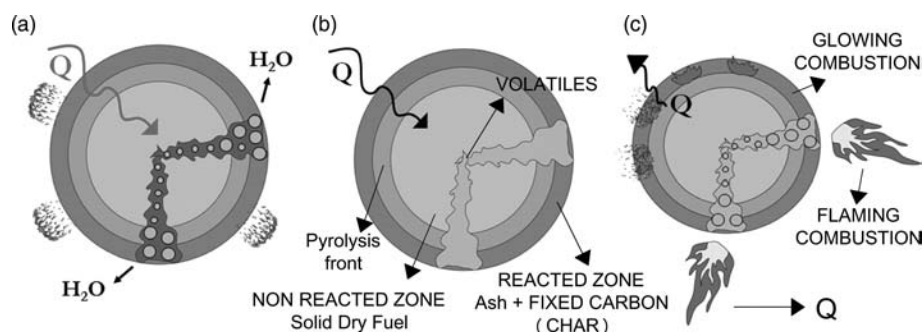


Figure 5.4. Schematization of the combustion of a solid biomass particle: (a) heating and drying; (b) devolatilization; (c) combustion.

(syngas) and vapors (tars) constitute the volatile content of the biomass and when ejected into the combustion chamber reacts with oxygen producing a flaming combustion.

Volatile extraction and combustion continues while the pyrolysis front moves towards the inner core of the particles, the same as the evaporation front did previously, leaving a charred layer on the outside which burns when in contact with oxygen. Char combustion does not produce a flame (glowing combustion) and it is particularly slow since oxidation happens only in the solid-gas boundary layer leaving a layer of insulating ashes which will eventually be removed by mechanical actions of the flue gases combined with gravity to allow oxygen to attack a new fresh layer of char.

This series of events which happen continuously during the combustion of a solid fuel, such as biomass, depends on the temperature reached by a certain area of the particle and on the exposure to oxygen, and are illustrated in Figure 5.4.

According to the temperature gradient the combustion of a solid fuel may then be divided into four steps that occur at different temperatures (Williams *et al.*, 2012):

STEP 1: Below 200°C (heating and drying) biomass absorbs heat in the heating and drying process. The sample loses weight steadily, but it does not ignite.

STEP 2: From 200°C to 280°C (torrefaction) the sample continues to increase its temperature while releasing preliminary volatiles deriving from low temperature decomposition, mainly hemicellulose; gases evolved are still not fully ignitable, however some exothermic reactions happen. The temperature at which the reaction of pyrolysis and oxidation become exothermic can be considered as the definition of the ignition point of wood. There are several studies examining the ignition point (Janssens, 1991; Li and Drysdale, 1992; Masafik, 1993; Fangrat *et al.*, 1997; Babrauskas, 2001) that could be considered to happen at a temperature of around 250°C.

STEP 3: From 280°C to 500°C (pyrolysis and volatile combustion): pyrolysis is the thermal degradation of a solid in the absence of oxygen; the global pyrolysis combustion model is represented in Figure 5.5. Pyrolysis is a process that is mainly endothermic and happens in two phases:

- the primary reactions are endothermic reactions that transform biomass in GAS (syngas), CHAR (fixed carbon + ashes) and TAR (condensable gases);
- the secondary reactions are exothermic reactions (cracking) that break tar in syngas and char.

During this phase pyrolysis gases copiously evolve from the particle and when they meet oxygen they burn with a flaming combustion in the gas phase, provided that the mixing with air happens within the lower and upper limits of flammability (LaGrega *et al.*, 1994). Self-sustaining diffusion flames from biomass can burn at 1100°C and more; one-half to two thirds of the heat of combustion is due to flaming combustion, the rest to glowing combustion of char. If pyrolysis

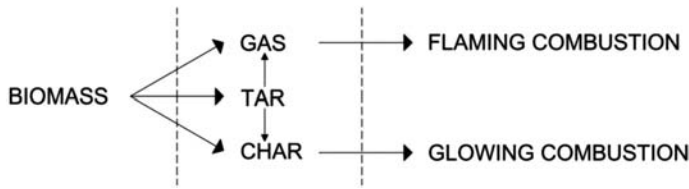


Figure 5.5. Simplified pyrolysis and combustion process (Tillman, 1991).

gases are liberated rapidly they consume oxygen around the particle surface therefore there is no oxygen left for char combustion which then accumulates.

Since char has only one-third to one-half the conductivity of wood (Browne, 1958) the layer of char decreases the progress of the pyrolysis front towards the inside of the particle (Fig. 5.5) and a temperature decreasing trend is observed passing from the surface of the particle to the center. This turns into a diversified timing of combustion within the particle which may be still expelling water from the inside core while the mid core is pyrolyzing and the outer layer is already charred. For this reason usually a strong initial flaming is followed by a decrease until sufficient heat has reached a deeper portion of wood to activate pyrolysis reaction.

STEP 4: above 500°C: Glowing combustion begins and it occurs with and without flame. When the surface temperature has reached 1000°C the char at the surface reacts as fast as the pyrolysis layer moves to the center of the particle (Martin, 1956). The luminous diffusion flames due to primary pyrolysis gases and tars are substituted by non-luminous diffusion flames due to the combustion of carbon and hydrogen. When even the production of those gases is ended the remaining char glows almost without flame.

The four steps of biomass combustion will be described with more detail in the following sections.

5.2.2 Heating and drying

The fuel particle can be simplified as a sphere that undergoes an endothermic process that is regulated by the equation of thermal exchange (Tillman, 1991):

$$Q = (\lambda \times A)/r \times (T_1 - T_2) \quad (5.13)$$

where:

λ = thermal conductivity [W/mK]

A = area [m²]

r = radius [m].

The temperature of the process varies, as a function of three steps:

- (i) *heating* from ambient temperature to 105°C, to reach evaporation temperature that is higher than 100°C because of inter-molecular forces that bind water inside the woody cell;
- (ii) *drying at 105°C*: this is an isothermal phase in which water leaves the woody particle, the evaporation front moves to the center of the particle generating a series of pores through which water and volatiles produced by pyrolysis will pass. The drying will continue until all the water contained in the biomass will evaporate. It is not a simultaneous process for all the layers of the sphere; in particular the external layer undergoes an immediate drying and it is not affected by pyrolysis but undergoes immediate combustion generating a layer of ashes that isolates from oxygen and heats the particle; the steam escaping from the particle contributes to the evacuation of ashes from the particle.
- (iii) *heating at temperatures higher than 105°C*. The heat is exchanged to particles through:
 - Radiation: from the flame and from the walls of the combustion chamber;
 - Conduction: from adjacent particles and from the walls of the combustion chamber;
 - Convection: due to turbulence and convective motions inside the combustion chamber.

As a result of this phase:

- (i) the wood particle shrinks by 7–17% in volume (Haygreen and Bowyer, 1982) and the material begins to crumble and crack; this produces an important reduction of the size (shrinkage) of the fuel;
- (ii) the diameter of the fuel pores also decreases reaching even 5–10 Å (Skaar, 1972).

The governing equation of the drying phenomenon is Ficks second law of diffusion (Chen *et al.*, 2012):

$$\frac{\partial MR}{\partial t} = \nabla(D_{eff}(\nabla MR)) \quad (5.14)$$

where:

MR represents the moisture ratio of biomass (Vega-Gálvez *et al.*, 2011), expressed by the following equation: $MR = (M - M_e)/(M_0 - M_e)$ where M_0 is the initial moisture content of the sample and M_e is the equilibrium moisture content of the sample

D_{eff} represents effective diffusivity of moisture [m^2/s] (Vega-Gálvez *et al.*, 2010).

Effective diffusivity (D_{eff}) is generally determined using experimental drying curves; on the other hand the temperature dependence of the effective moisture diffusivity can be represented by an Arrhenius relationship and derived using TGA analysis:

$$D_{eff} = D_0 \exp\left(-\frac{E_a}{R(T + 273.15)}\right) \quad (5.15)$$

where:

D_0 = pre-exponential factor of the Arrhenius equation [m^2/s]

E_a = activation energy for the moisture diffusion [kJ/mol]

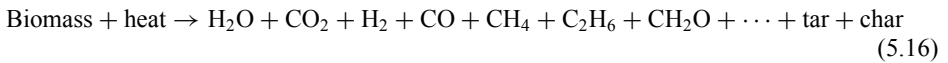
R = ideal gas constant [$J/mol \times K$]

T = drying temperature [$^{\circ}C$].

The activation energy can be calculated by plotting $\ln(D_{eff})$ vs. the reciprocal of the temperature $1/(T + 273.15)$.

5.2.3 Pyrolysis and devolatilization

Once all the moisture is evaporated and particle temperature has reached the pyrolysis threshold (about $280^{\circ}C$, as above mentioned) the devolatilization/pyrolysis process begins. The pyrolysis reaction can be generally represented by the following equation:



During the devolatilization phase a wide range of gaseous products are released through the decomposition of fuel (Fig. 5.6). The gaseous products most commonly produced by hemicellulose (composed by pentoses – such as xylan- and hexoses – d-glucose, d-galactose etc.) are: acetic acid, formaldehyde, carbon monoxide, hydrogen, but also furfural and furan. The first step in cellulose pyrolysis is the production of active cellulose (Browne, 1958; Sullivan and Ball, 2012; Liao and Ma, 2004), then if reaction temperature is low, activated cellulose will produce charcoal by dehydration.

As temperature increases, active cellulose will produce mainly levoglucosan (LG) and its isomeric anhydrosugar by cracking of glucosidic bonds at the same time the opening of acetal structural rings and cracking of internal carbon-carbon bond in pyroanoid rings will bring into the formation of hydroxyl-acetaldehyde (HAA), acetol, furfural, CO and other compounds. If secondary reactions happen then anhydrosugar will undergo a reaction similar to the opening and reforming of pyroanoid ring, producing small molecule gas and secondary char.

Lignin pyrolysis produces aromatic compounds and char. The production of char is higher if compared to cellulose. The initial breakdown during pyrolysis affects the straight chain links

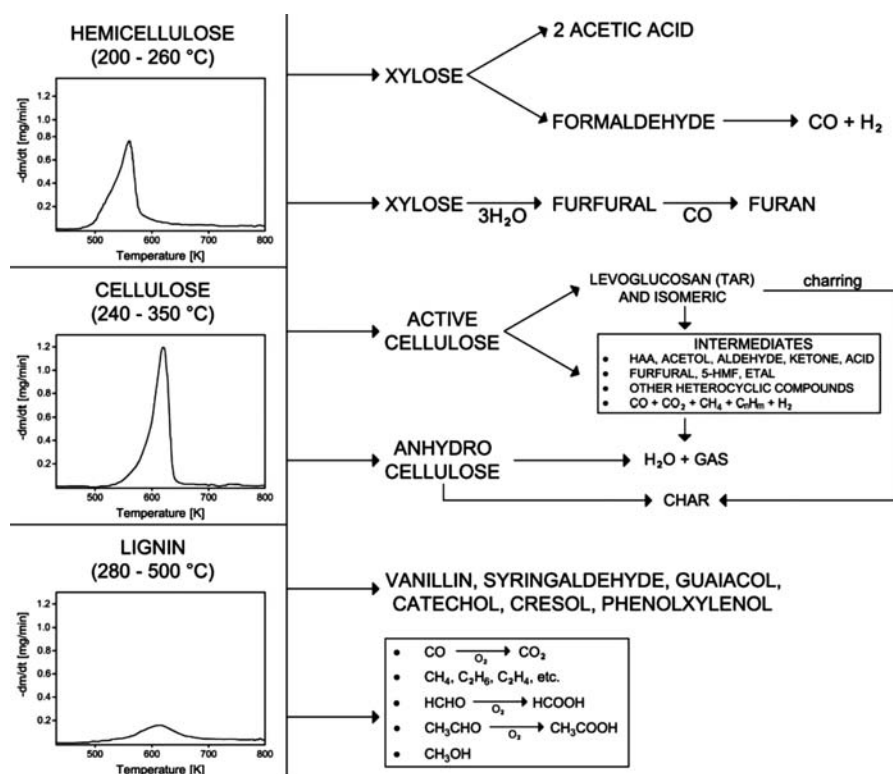


Figure 5.6. Pyrolysis and devolatilization mechanism.

Table 5.3. Pyrolysis kinetic constants for main biomass components (Anca-Couce *et al.*, 2012).

Component	E [kJ/mol]	Log A [log s ⁻¹]	n [-]
Wood	107	6.50	0.91
Cellulose	146	9.71	0.59
Hemi-cellulose	116	8.07	1
Lignin	167	11.3	2.78

which connect aromatic units such as: vanillyl, syringyl, guaiacols, cresols and catechols. The aromatic chains produce phenols, xylenols, guaiacols, cresols and catechols. The straight-chain links produce carbon dioxide, hydrocarbons, formic acid, acetic acid, higher fatty acids and methanol.

The development of biomass pyrolysis depends both on chemical and physical processes, so pyrolysis modeling is based on two approaches taking into account both *kinetics rates* and *heat transfer rates* (Di Blasi, 2008, Slopiecka *et al.*, 2012). Some examples of pyrolysis kinetic values are proposed in Table 5.3.

5.2.4 Char oxidation (glowing or smoldering combustion)

The products of pyrolysis that come in contact with oxygen will undergo two kinds of combustion: glowing combustion (char oxidation) and flaming combustion (volatiles oxidation).

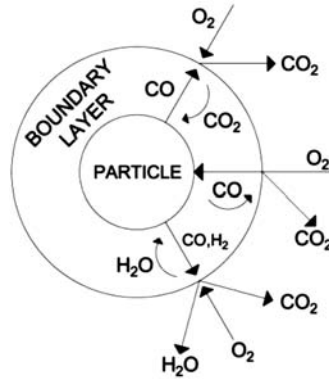
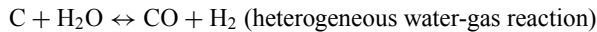
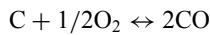


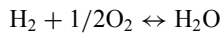
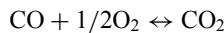
Figure 5.7. Schematization of char oxidation (Spliethoff, 2010).

Char oxidation is based on the reaction scheme shown in Figure 5.7.

Inside the particle or in the surface, oxygen, carbon dioxide and water vapor act as oxidants in the heterogeneous oxidation reactions:



In the gaseous phase the following homogeneous reactions happen:



Char combustion reaction is influenced both by combustion kinetics and mass transport processes in which the limiting process depends essentially on temperature. As a function of temperature three areas can be distinguished (Fig. 5.8):

- chemical reactions (low temperature);
- pore diffusion (temperature rises);
- boundary film diffusion (high temperatures).

Combustion reactions generate very high temperatures on the surface of char particles (1370–1650°C). With increasing temperatures the production of CO overcomes the production of CO₂. For example at 1027°C the ratio between the production of CO and CO₂ ranges from 5:1 to 21:1 (Matsui *et al.*, 1986). The cause of the increase in production of CO is the limiting step in char oxidation represented by oxygen diffusion to the char particle surface. Carbon oxidation becomes a two-step reaction: first CO is produced and then it is oxidized away from the char particle.

Char combustion is exothermic ($\Delta H \sim 32 \text{ kJ/kg}$), the activation energy is around 180 kJ/mol and the frequency factor is around $1.4 \times 10^{11} \text{ s}^{-1}$. Char combustion results to be slower than volatiles combustion, which is why much of the char oxidation occurs after flaming combustion.

The overall reaction rate of char oxidation depends on oxygen partial pressure, expressed at atmospheric pressure, and the reaction order with respect to oxygen (n_{O_2}) (Anca-Couce *et al.*,

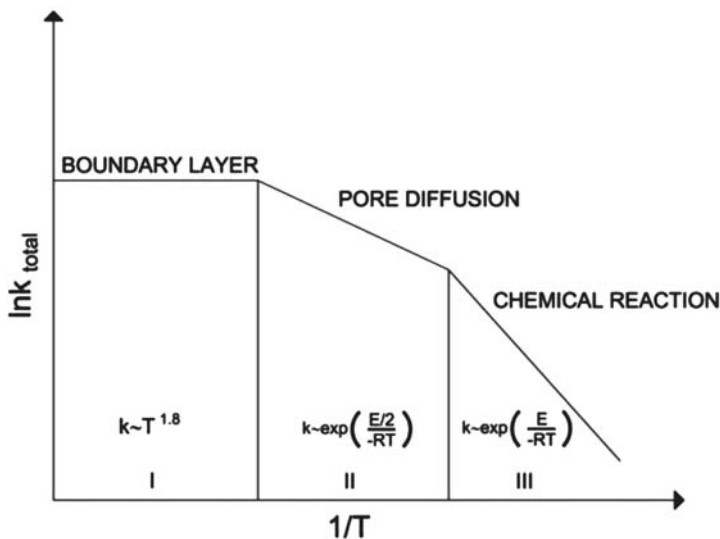


Figure 5.8. Schematization of char combustion areas (Spliethoff, 2010).

2012; Janse *et al.*, 1998):

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \left(\frac{X_{O_2}}{0.205}\right)^{n_{O_2}} \quad (5.17)$$

where:

- A = frequency factor [s^{-1}]
- E = activation energy [kJ/mol]
- R = gas constant [J/K mol]
- T = temperature [K]
- a = biomass conversion rate [–]
- X_{O_2} = partial oxygen pressure [Pa]
- n = reaction order with respect to oxygen [–].

Figure 5.9 shows a thermogravimetry for a generic biomass. The peaks d1, d2 and ch represent respectively the devolatilization step (d1 and d2) and the char oxidation step (ch), obtained through deconvolution of thermogravimetric data (Fig. 5.9). The activation energy and frequency factor reported in Table 5.4 can be used for SFOR models (single first order reaction models).

5.2.5 Volatiles oxidation (flaming combustion)

This process originates the visible flame following the reactions of flaming combustion. Oxidation happens generating a diffusive flame due to slow combustion because volatiles substances exiting form the particle and oxidizing agent are not pre-mixed.

As reported by (Miller and Tillman, 2008) during volatile oxidation different free-radical reactions happen, such as:

- chain initiation (it happens between volatile species and fragments evolving from the solid fuel matrix);
- chain propagation (it involves the previously formed reactive free radicals, such as hydroxyl radical);
- chain termination (that completes the process).

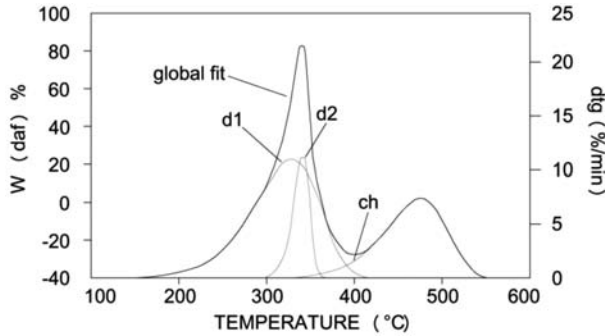
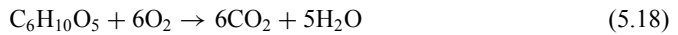


Figure 5.9. Thermogravimetric curve for biomass (Biagini and Tognotti, 2006).

Table 5.4. Char combustion rates for different biomasses (Biagini and Tognotti, 2006).

Fuel	Peak	E [MJ/kmol]	A [min^{-1}]
Wood pellet	d1	69	6.70×10^5
Wood pellet	d2	346	6.96×10^{29}
Wood pellet	ch	107	1.32×10^7
Pine wood	d1	75	1.62×10^6
Pine wood	d2	344	2.90×10^{29}
Pine wood	ch	129	5.05×10^8
Cacao residue	d1	146	7.33×10^{15}
Cacao residue	d2	51	1.80×10^4
Cacao residue	ch	120	9.20×10^7

A simple chemical equation for levoglucosan combustion is the following (Sullivan and Ball, 2012):



Besides the stoichiometric equation it has to be considered that several intermediate compounds are created during flaming combustion of the volatiles. Woodley (1971) has identified about 40 compounds, produced by the thermal degradation of levoglucosan.

The oxidation reactions are exothermic and very fast. The activation energy for the oxidation of levoglucosan is about 190 kJ/mol, the frequency factor is about $2.55 \times 10^{13} \text{ s}^{-1}$. The reaction enthalpy for complete combustion is -14 kJ/g (Parker and LeVan, 1989).

Some other gas phase homogeneous reactions are reported in the following Table 5.5.

5.2.6 Combustion rates, flame temperature and efficiency

Combustion time, defined as “total time for burnout of the particle” (Tillman, 1991) can be calculated with the following formula:

$$t_{bo} = t_d + t_p + t_{co} \quad (5.19)$$

where:

- t_{bo} = total burnout of the particle
- t_d = time for heating and drying
- t_p = time for solid particle pyrolysis and
- t_{co} = time for char oxidation.

Table 5.5. Some relevant gas-phase homogenous reactions (Haseli *et al.*, 2011).

Reaction	Source	Reaction rate expression	Kinetic parameters
$\text{CH}_4 + 1.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$	Dryer Glassman (1973)	$r_{\text{CH}_4} = -10^n \times C_{\text{CH}_4}^{0.7} \times C_{\text{O}_2}^{0.8} \times \exp\left[-\frac{E \times 4.18}{R \times T}\right] \times 10^{-4} [\text{s}^{-1}]$	$n = 13.2 \pm 0.2$ $E = 48400 \pm 1200 [\text{cal} \cdot \text{mol}^{-1}]$
$2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$	De Souza Santos (1989; 1994; 1987)	$r_{\text{H}_2} = \frac{K}{T_g^{1.5} [y_{\text{H}_2}^{1.5} y_{\text{O}_2} \rho_g^{2.5}]} [\text{s}^{-1}]$	$K = 5.159 \times 10^{15} \exp(-3430/T_g)$ $[\text{kmol}^{-1.5} \text{m}^{4.5} \text{K}^{1.5} \text{s}^{-1}]$
$\text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2$	Dryer Glassman (1973)	$r_{\text{CO}} = -10^n \times C_{\text{CO}} \times C_{\text{O}_2}^{0.25} \times C_{\text{H}_2\text{O}}^{0.5} \times \exp\left[-\frac{E \times 4.18}{R \times T}\right] \times 10^{-4.5} [\text{s}^{-1}]$	$n = 14.75 \pm 0.4$ $E = 43000 \pm 2200 [\text{cal} \cdot \text{mol}^{-1}]$
$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$	De Souza Santos (1989; 1994; 1987)	$r = k \left[y_{\text{CO}} y_{\text{H}_2\text{O}} - \frac{y_{\text{CO}_2} y_{\text{H}_2}}{K^*} \right] [\text{s}^{-1}]$	$K = 2.78 \times 10^3 \exp(-1510/T_g)$ $[\text{kmol}^{-1} \text{m}^3 \text{s}^{-1}]$ $K^* = 0.0265 \exp(3968/T_g) [-]$

Table 5.6. Thermochemical data for cellulose combustion (Di Blasi, 1993; Antal and Várhegyi, 1995; Branca and Di Blasi, 2004; Parker and LeVan, 1989).

Reaction	Activation energy [kJ/mol]	Frequency factor [s ⁻¹]	Reaction enthalpy [kJ/g]	Product	Reference
Charring	110	6.7×10^5	-1.0	Char formed	Di Blasi (1993)
Volatilization	198	3.2×10^{14}	0.3	Volatiles formed	Antal and Várhegyi (1995)
Char oxidation	183	1.4×10^{11}	-33	Char oxidized	Branca and Di Blasi (2004)
Volatile oxidation	188	2.6×10^{13}	-14	Volatiles oxidized	Parker and LeVan (1989)

The evaluation of combustion times can be done also with single particle combustion models. Besides important effort in the research of modeling of single particle combustion has been done (Yang *et al.*, 2008) and some models evaluate also particle burnout (Saastamoinen *et al.*, 2010). The combustion rate or burning rate can be considered as the mass of fuel consumed per unit of time. This influences heat release and so this parameter is important for the design of the combustion system. Typical design heat release rates, expressed per unit grate area, are 2–4 MW_t/m² (Brown, 2011), even though some fluidized beds can reach 10 MW_t/m² (Jenkins, 1998). Combustion rates can be calculated starting from some thermochemical data, such as those shown for cellulose in Table 5.6 (Sullivan and Ball, 2012).

The reaction of charring starts with hydrolysis of cellulose and then continues with dehydration, decarbonylation, decarboxylation cross-linking and aromatization reactions to produce primary char.

The volatilization reactions of cellulose can be thought as the formation of levoglucosan, while char oxidation and volatile oxidation complete the combustion process. As has been previously discussed the more important reaction from the point of view of combustion velocity control is char oxidation influenced by oxygen penetration inside the particle. This is why for practical and engineering purposes the most adequate formula to express the burning rate is that proposed by Kuo (1998). Kuo's method is based on the assumption that solid fuel bed-burning rate is proportional to the oxygen consumption rate as air flows through the fuel bed.

Knowing that oxygen distribution in the fuel bed can be represented as:

$$\frac{dX_{O_2}}{dy^*} = -\hat{K} X_{O_2}^n (1 - a_r X_{O_2}) \quad (5.20)$$

where:

$\hat{K} = -(R_d/a_r)\ln(1 - a_r X_{O_2})$: average reaction rate [-]

$R_d = a_p L \times j_D S_C^{-2/3}$: coefficient of reaction rate [-]

n = order of reaction [-]

a_r = ratio of change in gaseous moles to the change in oxygen moles [-].

The combustion rate can be calculated as follows:

$$B_G = (1/r_{af})(1 - (a_1 X_{O_2,b}/(1 - a_r X_{O_2,b})))G_{air} \quad (5.21)$$

where:

$X_{O_2,b}$ = mole fraction of oxygen in product gas leaving the fuel bed

$a_1 = 4.76 - a_r$

$\hat{r}_{afv} = 4.76\hat{r}_{of}$ is the stoichiometric air-to-fuel mole ratio

G_{air} = mass flux of the air flowing through the refuse bed [$\text{kg}/\text{m}^2/\text{h}$].

By comparing the bed-chemistry model and the operating data of a large incineration facility of municipal solid residue, Kuo (1998) showed that n is equal to 1 and R_d could be in the range between 10 and 40 depending upon the average under-grate air-flowrate.

Flame temperature for biomass fuels can be calculated with the following formula (Tillman, 1991):

$$T_f (^\circ\text{F}) = 3870 - 15.6(MC) - 130.4(E_{O_2}) + 0.59(T_a - 77) \quad (5.22)$$

where:

MC = moisture content of the material on a wet basis [%]

E_{O_2} = percentage of excess oxygen in the flue gas (total basis) [%]

T_a = combustion air Temperature [$^\circ\text{F}$].

The combustion adiabatic flame temperature has to be adjusted taking into account heat losses. Gaydon and Wolphard (1979) have supposed a correction factor of 0.8. Other possible coefficients could be: 0.8–0.9 for water wall units and 0.9–0.95 for refractory lined units.

To work with high combustion temperature is not optimal because it will result in high production of NO_x and possible ash melting. Temperature control through the manipulation of combustion mechanism is of fundamental importance to optimize combustion efficiency and combustion emissions.

This could be done through:

- governing the rate of heat removal in in-bed tubes for energy recovery, through extensive heat transfer walls in fluidized beds, etc.;
- manipulation of stoichiometric ratio (moles O_2 /mole fuel) or equivalence ratio (moles fuel/moles O_2);
- manipulating the oxidant composition (moles O_2 /mole N_2), largely through oxygen enrichment temperature);
- manipulating the temperature of the oxidant (i.e. preheating the air to levels above ambient temperature);
- manipulating the calorific value of the fuel expressed in higher and lower heating value;
- manipulating the moisture content of the combustion atmosphere, governed either by the moisture content of the fuel or by the water or steam injection into the system.

Dealing with the heat released during combustion, the combustion efficiency has to be considered, that is, the ratio between the input energy (heat and/or work utilized) and the energy

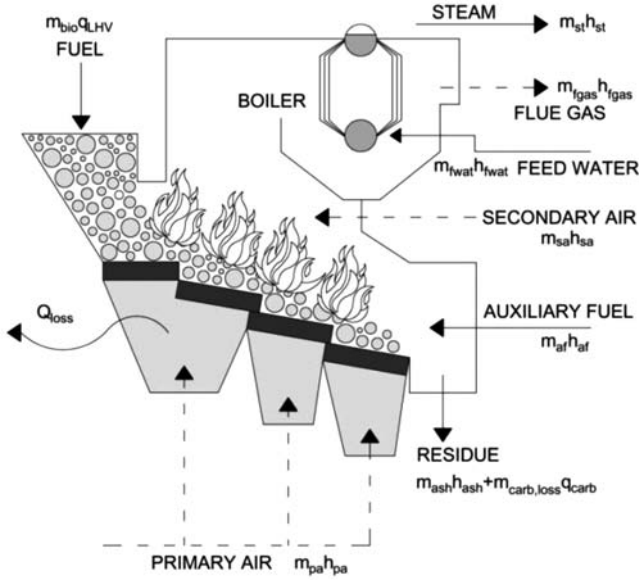


Figure 5.10. Biomass combustor model (Hsi and Kuo, 2008).

obtained. The direct calculation of the combustion system efficiency can be made if the conditions of the exchanging fluids are known (for example steam in the case of a steam boiler). The indirect calculation of the combustion system efficiency (η) can be done only taking into account the losses:

$$E_{in} = E_{out} + E_{lost}$$

$$\eta = \frac{E_{out}}{E_{in}} = 1 - \frac{E_{lost}}{E_{in}}$$

With reference to Figure 5.10 the combustion systems efficiency may be defined considering the following energy balance for a furnace-boiler:

$$\dot{m}_{bio} q_{LHV} + \dot{m}_{fuel} q_{fuel} + \dot{m}_{pa} h_{pa} + \dot{m}_{sa} h_{sa} + \dot{m}_{fwat} h_{fwat} = \dot{m}_{st} h_{st} + \dot{m}_{fgas} h_{fgas} + \dot{m}_{ash} h_{ash} + \dot{m}_{carb, loss} q_{carb} + \dot{Q}_{loss} \quad (5.23)$$

where:

- $\dot{m}_{bio}$ = biomass mass flow [kg/h]
- q_{LHV} = lower heating value of biomass [kJ/kg]
- $\dot{m}_{fuel}$ = auxiliary fuel mass flow [kg/h]
- q_{fuel} = heating value of auxiliary fuel [kJ/kg]
- $\dot{m}_{pa}$ = primary air mass flow [kg/h]
- h_{pa} = specific enthalpy of primary air [kJ/kg]
- $\dot{m}_{sa}$ = secondary air mass flow [kg/h]
- h_{sa} = specific enthalpy of secondary air [kJ/kg]
- $\dot{m}_{fwat}$ = boiler feed water mass flow [kg/h]
- h_{fwat} = specific enthalpy of boiler feed water [kJ/kg]
- $\dot{m}_{st}$ = steam mass flow [kg/h]
- h_{st} = specific enthalpy of steam [kJ/kg]
- $\dot{m}_{fgas}$ = exhaust gas mass flow [kg/h]
- h_{fgas} = specific enthalpy of exhaust gas [kJ/kg]
- $\dot{m}_{ash}$ = ashes mass flow [kg/h]

- h_{ash} = specific enthalpy of ashes [kJ/kg]
 $\dot{m}_{carb, loss}$ = unburned carbon mass flow [kg/h]
 q_{carb} = heating value of unburned carbon [kJ/kg]
 Q_{loss} = heat loss outwards from the furnace/boiler system [kJ/h].

$$m_{bio} = \left(\dot{\rho}_{air} \hat{M}_B / \hat{M}_{air} \right) (\dot{F}_{pa} + \dot{F}_{sa}) / (4.76 (1 + \varepsilon) \hat{r}_{of})$$

where:

- $\dot{F}_{pa}$ = primary air flow rate [Nm³/h]
 $\dot{F}_{sa}$ = secondary air flow rate [Nm³/h]
 $\dot{\rho}_{air}$ = air density [kg/m³]
 $\hat{M}_B$ = molecular weight of biomass [-]
 $\hat{M}_{air}$ = molecular weight of air [-]
 ε = excess air ratio [-]
 $\hat{r}_{of}$ = stoichiometric oxygen-to-fuel mole ratio [-].

5.3 COMBUSTORS

5.3.1 Introduction to biomass combustion systems

Combustion is an exothermic reaction that releases the chemical energy (*HHV*) of a fuel transforming it into heat that is transferred to the surrounding environment (combustion chamber) and to the combustion products (flue gases and ashes) (Oberberger, 1998). Combustion of a solid fuel is actually carried out as the exothermic release of the chemical energy contained in two different fuels: a volatile fuel mixture of permanent gases (syngas) and vapors (tars) which burns rapidly in the gaseous phases (volatile matter) and a carbonaceous solid fuel (char) which burns slowly in the solid-gas interface. However these two different fuels must be extracted from the original solid fuel and this is accomplished in the preliminary phases (heating, drying and pyrolysis) providing thermal energy (heat) to the feedstock.

A combustor device for solid fuels must then be designed to guarantee an adequate heat exchange between the feedstock and the reactor in order to allow drying and extraction of volatile matter within the residence time. Since the two fuels obtained have different combustion behavior being respectively a gas (volatiles) and a solid (char) the oxidant (usually air) must be provided in different quantities and in different places inside the reactor to guarantee complete combustion.

Char glowing combustion is carried out in the boundary layer between the solid surface and the gaseous phase and therefore it requires an active surface available for oxygen to combine with carbon. The external layer of each particle is burnt leaving an ash deposit which partly shields the new active layer of carbon from further oxidation. Char combustion is then slowed by the incomplete availability of new active layers of carbon due to its solid geometry and ash deposits. Combustion air to oxidize char is called primary air or underfire air because it must be provided within the feedstock bed with an adequate velocity to optimize turbulence and mechanical stress on the particle for ash removal. It will also be provided in high excess with respect to stoichiometric conditions given the disadvantaged mixing conditions between fuel and oxidant.

Considering the previous general mass composition of biomass and a generic content x [kgC/kg_{bio,db}] of fixed carbon in the dry feedstock the following equation provides the primary air mass flow:

$$R_p \times x \times 32/12 \times 100/23.3 \quad [\text{kg air/kg fixed carbon}] \quad (5.24)$$

where R_p [kg_{air}/kg_{air,st}] is the ratio between the mass of primary combustion air provided and the theoretical stoichiometric primary combustion air.

Volatiles flaming combustion, on the other hand, takes place in the gaseous phase above the solid fuel bed and it is fairly more advantaged with respect to char combustion, given the high

miscibility of fuel gases and gaseous oxidant. Combustion air to oxidize volatile products is called secondary air or overfire air because it must be provided above the solid fuel bed with an adequate turbulence to guarantee adequate mixing with the gaseous fuel.

As considered in section 5.2, given the generic biomass mass composition $C_p H_q O_r$, the following quantity represents the stoichiometric amount of air needed to oxidize hydrogen:

$$(8q - r) \times 100/23.3 \quad [\text{kg air/kg H}] \quad (5.25)$$

While the following quantity represents the stoichiometric amount of air needed to oxidize volatile carbon:

$$(p - x) \times 32/12 \times 100/23.3 \quad [\text{kg air/kg volatile carbon}] \quad (5.26)$$

Therefore the following equation provides the secondary air mass flow:

$$R_s \times ((8q - r) \times 100/23.3 + (p - x) \times 32/12 \times 100/23.3) \quad [\text{kg air/kg volatile matter}] \quad (5.27)$$

where $(\text{kg}_{\text{air}}/\text{kg}_{\text{air,st}})$ is the ratio between the mass of secondary combustion air provided and the theoretical stoichiometric secondary combustion air.

The sum of primary air and secondary air mass flows represents the total combustion air:

$$R_s \times 100/23.3 \times ((8q - r) \times p \times 32/12) + x \times (R_p - R_s) \times 32/12 \times 100/23.3 \quad [\text{kg air/kg biomass}] \quad (5.28)$$

which was already determined in 5.2 for stoichiometric conditions, and which can be easily obtained from the previous when considering $R_p = R_s = 1$.

Combustion performance depends strongly on the geometry of the reactor, on the air and fuel inlet and resulting turbulence inside the reactor and also on the size of the solid fuel given that the ratio between external surface of the particles, which determines the heat exchange rate and char oxidation rate and the particle volume increase with decreasing particle size. Adequate heat transfer to the solid fuel and char/volatiles mixing with air is also guaranteed by an adequate movement of the fuel inside the reactor, which must also provide a pathway for ash removal from the combustion chamber.

Biomass combustion may be used in a power cycle for CHP application or to provide process heat in a boiler or for heating and air conditioning for households or larger scale applications. Whatever the application the general process scheme would be the one in (Figure 5.11) where a generic feedstock is burnt, flue gases are cleaned of particulates in a dedicated device (e.g. cyclone) and flow into a heat exchanger providing heat to a working fluid which runs a power cycle for CHP or is conveyed directly to a thermal user. Given the relatively high biomass ash content and their possible low melting point, usually the heat exchanger is not installed directly inside the combustion chamber and it is not directly exposed to the flame to avoid high temperature corrosion and fouling of the tubes. Cooled gases are then conveyed to the emission abatement section, which can be as simple as a filter for particulate matter, and eventually reach the stack.

As described by various authors (Baukal, 2004), there are four mainly diffused typologies of biomass combustors: pile burners, grate burners, suspension burners and fluidized bed burners; depending on the application (industrial or household) the concept may be modified to fit the different size of the combustion chamber.

Pile and grate burners are often referred to as fixed bed combustors while suspension and fluidized bed burners are often referred to moving bed combustors. Their different concept and performance will be described in the following sections.

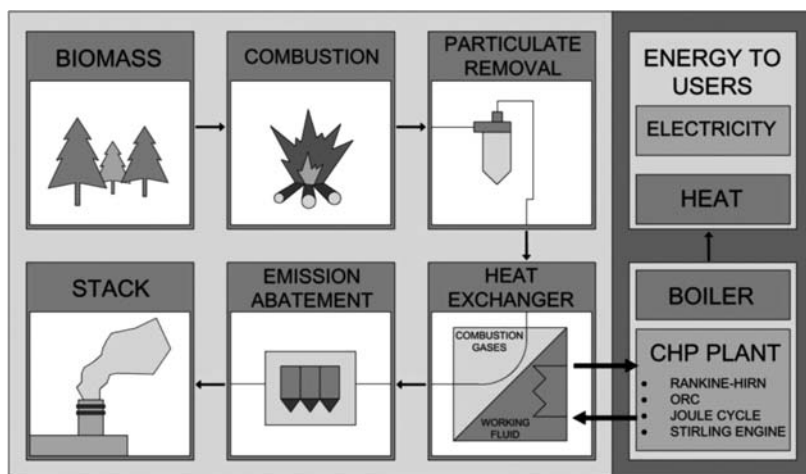


Figure 5.11. Process scheme for biomass energy recovery through combustion.

5.3.2 Fixed bed combustion

As mentioned above, fixed bed combustion is one of the most used technologies in biomass combustion thanks to the following advantages: it can fire a wide range of fuels (of varying moisture content, particle size and ash content) and requires less fuel preparation and handling. Fixed bed combustors usually consist of a two-stage combustion chamber with a separate furnace and boiler located above the secondary chamber where the oxidation of volatilized products is completed. They can be divided into pile burners and grate burners.

5.3.2.1 Pile burners

The simplest technology for biomass combustion is the pile burner which is the engineered version of the primitive bone fire solution. Biomass is piled inside a refractory chamber through a screw conveyor, in an underfeed system, or dropped on top of the pile in overfeed systems (Fig. 5.12) and it is ignited manually or with an oil or gas start-up burner. Primary air is blown directly inside the bed through holes in the refractory lining while secondary air is provided above the bed through chute openings. Combustion is mainly surface driven, therefore adequate radiation from the combustion chamber walls is necessary and vaulted ceilings are usually utilized. The conical pile settles according to the friction angle of the material and in underfeed burners new fuel pushes inside the pile causing a bottom-up vertical gradient of the mass loss and the ashes on top to fall at the sides of the pile where the ash pits are located. In overfeed burners no forced movement of the pile is present and a gravity driven top-bottom gradient of mass loss is present causing the ashes to fall into the ash pit which is positioned below the bed.

Ash is usually removed from the ash pit by manually extracting the container as a drawer, or else by cleaning the grate directly when the ash is cooled. In either case the cyclic operation of the burner results in high maintenance requirements which contribute to the low efficiencies (<70%) and difficulties in controlling the process. Automated ash extraction through augers may be present in bigger scale applications to increase availability. Pile burners are not suitable for load following operation while they are simple, inexpensive and suitable to burn wet and dirty fuels.

A typical overfeed pile burner for small to medium scale application is the so called Dutch oven which is the oldest technology still in use, especially in the forestry products and sugar industry.

With reference to Figure 5.13 the Dutch-oven technology is a two-chamber furnace made of refractory walls with holes (tubes) for combustion air inlet and fuel is dropped on a grate from a

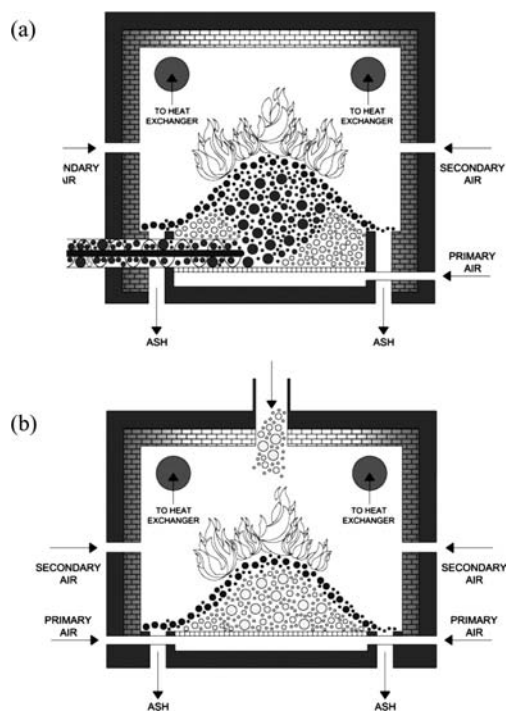


Figure 5.12. Working principle of (a) an underfeed pile burner and (b) an overfeed pile burner.

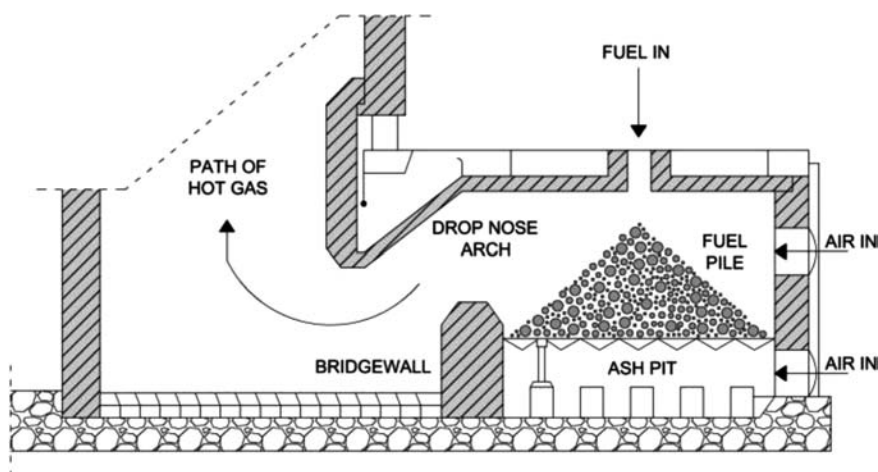


Figure 5.13. Working principle of an overfeed pile burner: Dutch-oven.

hole on the ceiling. Drying and gasification takes place in the first chamber where radiation from the walls and ceiling is essential to speed up the process. The construction characteristics vary considerably according to the different biomass size and humidity, although the Dutch-oven can handle easily fuel with up to 50% humidity thanks to the heat reservoir of the pile which however does not allow abrupt load changes.

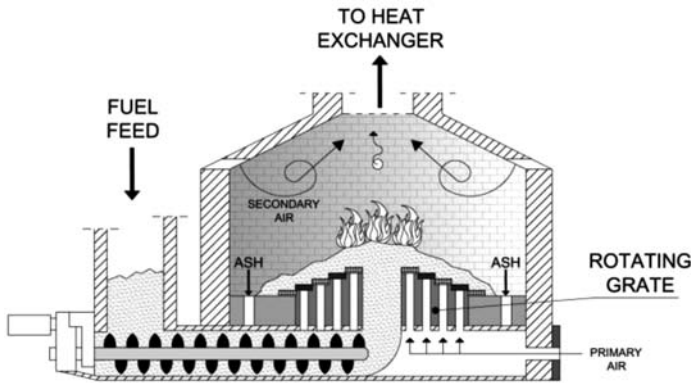


Figure 5.14. Working principle of an underfeed cyclonic furnace.

When a single chamber pile combustor is considered, the underfeed solution in a cylindrical combustion chamber is the so-called cyclonic furnace (Fig. 5.14) which is still used in northern Europe. Combustion gases are extracted from the top of the brick lined furnace and are conveyed to the heat exchanger while biomass is pushed by an auger through a hole at the center of a circular grate on top of which the pile is formed. For this reason the cyclonic furnace may also be considered as a grate combustor. During combustion the solid fuels proceeds radially from the center to the periphery where ashes are discarded. Primary air is fed preheated through the grate while secondary air is provided tangentially on the top of the furnace as to provide a cyclonic vortex that optimizes the combustion of volatiles. The cyclonic furnace shows a relatively high efficiency, also on wet fuels, and low dust emission while its disadvantages are mainly related to its high maintenance costs and poor automation possibilities.

5.3.2.2 Grate burners

Grate burners (Fig. 5.15) achieve a higher combustion velocity and efficiency, with respect to pile burners, because the solid fuel is evenly spread (not piled) on a grate by a dedicated device called a stoker, and this allows a better mixing between air and fuel. Moreover the fuel moves across the grate, from the inlet section to the ash discharge section, mechanically driven by the movement of the grate or by gravity; this increases the mixing of fuel and air and it facilitates the disruption of the solid char, which then burns more quickly. Moreover the movement of the fuel inside the combustion chamber allows a certain degree of differentiation in the air supply to different areas of the combustion chamber, which can then be adjusted according to the typical heating-drying-pyrolysis-oxidation sequence.

A scheme of a modern grate-fired boiler is composed of: a fuel feeding system, a grate assembly, a secondary air (including over-fire air or OFA) system and an ash discharge system (Yin *et al.*, 2008).

Typical fuel feeding and distribution systems are represented by mechanical stokers and spreader stokers which continuously propel fuel into the combustion chamber and above the grate. The smallest particles burn in suspension (if the fuel is very fine, i.e. 30% or higher then mass fraction has dimensions smaller than a few millimeters) while bigger pieces fall into the grate and form the fuel bed. The fuel feeding system regulates the amount of fuel which is fed to the furnace while the distributor evenly spreads the fuel on the grate. Typical feeding systems are positioned under a hopper and are either a conveyor belt, a piston, a screw conveyor or a rotary vane feeder, whose speed may be varied to regulate the fuel flow (dosing system). The rotary vane system provides also a physical isolation of the hopper from the combustion chamber preventing backfire and may also be used in combination with the other systems. From the feeding systems

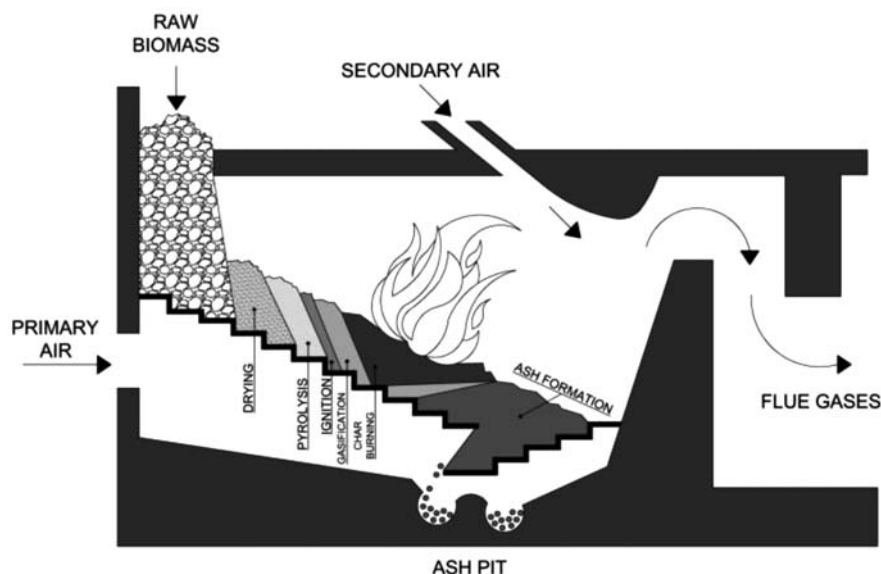


Figure 5.15. Working principle of a sloping grate combustor.

the solid fuel reaches the distributors which can be either mechanical or pneumatic (Fig. 5.16). In the first case a revolving device throws the fuel into the furnace while in the second case a pulsating high pressure air flow blows the fuel inside the combustion chamber and on the grate.

Capacities of grate-fired boilers range from 4 to 300 MW_t and are mainly grouped around 20–50 MW_t in biomass fired CHP plants. The heat release per grate area can be around 4 MW_t/m² (U.S. Environmental Protection Agency, 2007). The grate that is at the bottom of the combustion chamber has two main functions: to guarantee a homogeneous distribution of the fuel and of the bed of embers over the whole grate furnace, and equal distribution of air entering from beneath over the whole grate areas.

As far as the primary and secondary air supply systems are concerned, they play a very important role in the efficient and complete combustion of biomass. For grate-firing the overall excess air is about 25–50% (Nor'West-Pacific Corporation, 1981) and it can be considered that excess air equals the moisture content of the fuel. The ratio between primary air and secondary air tends to be 40/60. Primary air supply must be divided into sections in order to operate the grate furnaces at partial loads (down to about 25% of the nominal furnace load) and control the primary air ratio needed (to secure a reducing atmosphere in the primary combustion chamber necessary for low NO_x operation).

The fuel bed is composed of solid particles that are piled up with a characteristic porosity and it is heated by over-bed flames and refractory furnace walls until it ignites on the top surface of the fuel bed. The accepted combustion mechanism of cross current units considers that after ignition a reaction front propagates from the surface of the bed to the grate against the direction of primary air even if this traditional pathway may not be observed, depending on fuel properties and operating conditions (Saastamoinen *et al.*, 2000; Thunman and Leckner, 2001; Zhou *et al.*, 2005; Yang *et al.*, 2004). A reaction front propagating from the grate upwards to the surface of the bed was also reported. The reaction front then moves downward against the primary air flux and a char and has layer remains in the surface. When the reaction reaches the surface of the grate the availability of oxygen increases and char can be oxidized as well; glowing combustion takes the place of flaming combustion.

Inhomogeneous air supply may cause slagging and higher fly-ash amounts and may increase the excess oxygen needed for a complete combustion, resulting in boiler heat losses. To avoid

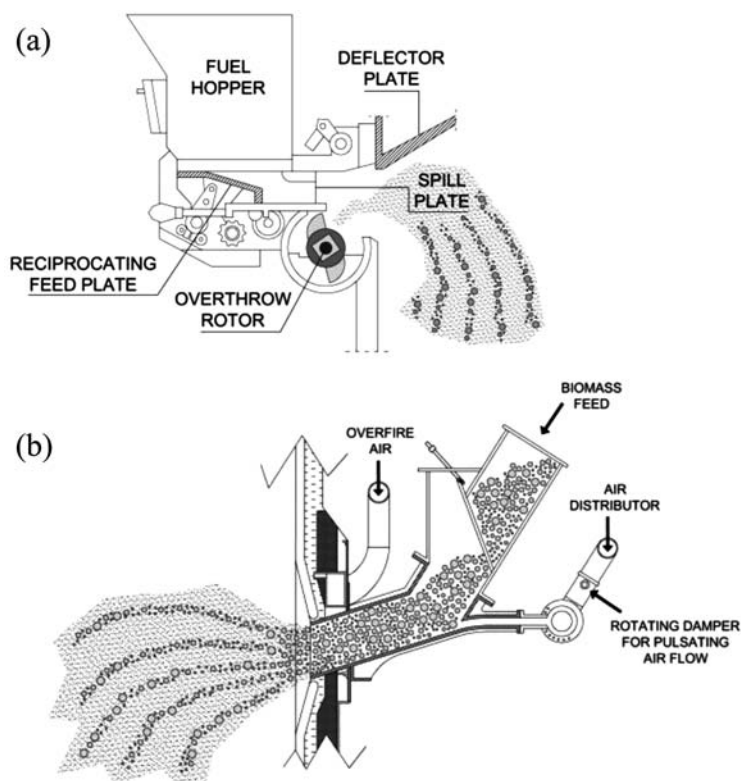


Figure 5.16. Working principle of a mechanical (a) and pneumatic (b) spreader-stoker.

this problem continuously moving grates, a height control system of the bed of embers (e.g. by infrared beams) and frequency-controlled primary air fans for the various grate sections can be used. Gases released by biomass conversion in the grate and a small amount of entrained fuel particle continue to burn over the bed and secondary air plays an important role in mixing, burnout and emissions.

An advanced secondary air supply system is one of the most important elements in the optimization of the gas combustion in the freeboard and it is an important retro-fit to improve burnout in old grate-fired boilers and reduce pollutant emissions.

Grates can be water-cooled (more indicated for dry biomass fuels with low ash-sintering temperatures) or air-cooled (more indicated for wet bark, saw dust and wood chips). Grate burners may be divided in two main categories (see Table 5.7) (Yin *et al.*, 2008; Van Loo and Kopperjan, 2002):

- *stationary grates*, where the grate is fixed with respect to the combustion chamber and fuel motion is driven by gravity; they are also called sloping grates;
- *moving grates*, where the grate moves with respect to the combustion chamber and the mechanical motion induced (vibration, alternate or translational) moves the solid fuel. Depending on the motion they are called vibrating grates, reciprocating grates and traveling grates.

In stationary sloping grates fuel is introduced on the top of the slope with mechanical or pneumatic distributors and it tumbles down the slope, which angle may be constant or varying according to the different velocity of combustion required at different stages. The grates consists

Table 5.7. Grate burners typologies and characteristics (Yin *et al.*, 2008; van Loo and Kopperjan, 2002).

Type of grate	Main characteristics
STATIONARY GRATES	
Sloping grate	– the grate does not move; – the fuel burns as it slides down the slope under gravity; – the control of combustion is difficult; – there is risk of avalanching of the fuel.
MOVING GRATES	
Traveling grate	– the fuel is fed on one side of the grate and is burned while it is transported to the ash pit; – the control and carbon burnout efficiency are improved.
Reciprocating grate	– the grate tumbles and transports fuel by reciprocating (forward-reverse) movements of the grate rods as combustion proceeds; – finally the solids are transported to the ash pit at the end of the grate; – carbon burnout is further improved due to better mixing.
Vibrating grate	– the grate has a shaking movement that spreads the fuel evenly; – this type has less moving parts than other movable grates; – carbon burnout efficiency is further improved; – vibrating grates have the longest life.
Underfeed rotating grates	– conical grate sections rotate in opposite directions and are supplied with primary air from below; – wet and burning fuels are well mixed (the system can work with very wet fuels); – combustible gases formed are burned out with secondary air in a separate horizontal or vertical combustion chamber; – the fuel is fed from below by screw conveyors (similar to underfeed stokers); – the fuel moves to the periphery of the circular grate, at the edge of the grate ash falls into a water-filled ash basin underneath the grate.

of steel cast alloy blocks, which may be water-cooled, and evenly spaced to form either a flat surface or a staircase. Water cooling may be used to increase the life length of the grate and also to reduce the local temperature where ash is formed to avoid ash melting and slagging problems.

Primary combustion air is provided in excess with respect to stoichiometric conditions through pin holes in the grate blocks and may represents up to 75% of the overall combustion air. Alternative solutions for air supply consider integral fins where holes are protected by deflector plates welded to the fins to prevent fines from plugging the holes and to direct the air down the slope and help the advancement of ashes towards the ash pit. Stationary grates (Fig. 5.17) require periodical manual cleaning of the grate from ashes, since the slope and air jets are not sufficient to move all the ashes to the pit, however, much less than in pile burners. The remaining 25% of combustion air is provided as secondary over-fire air from ports in the brick wall.

Moving grates have a different configuration according to the different mechanical principle that moves the bars of the grate.

In vibrating grates a rapid oscillatory motion of the elements facilitates the movement of the solids throughout the combustion chamber and the sliding across the grate which is usually a slope with a fixed angle. The compacting action of the vibrations allows a wide range of fuels to be burnt with a maximum thermal load around 2500 kW/m².

In reciprocating grates it is the alternate motion of the moving segments, either forward-backwards on sloping grates or an angular tilting on horizontal grates, that pushes solids throughout the grate and also the ashes to the ash pit. The moving bars are positioned between fixed ones and are attached to a frame which is activated by a hydraulic system slowly and intermittently. The frequency and width of the strokes allow adjustment of the fuel layer to optimize combustion and emissions. Under-fire primary air is provided through the gaps between movable and fixed bars.

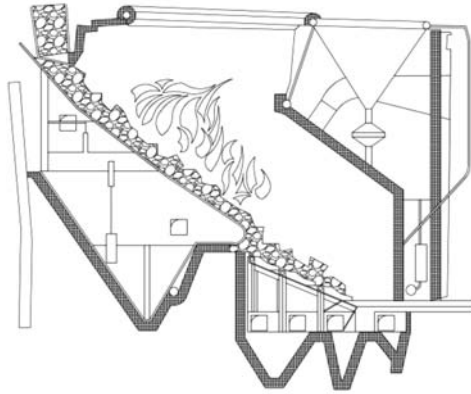


Figure 5.17. Cross section of a stationary sloping grate (Tillman, 1991).

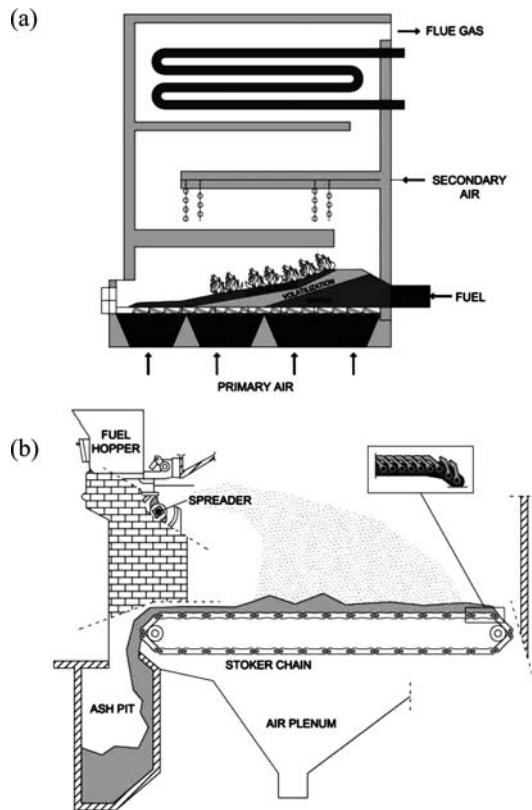


Figure 5.18. Working principle of a reciprocating horizontal grate (a) and traveling grate (b).

In a traveling grate the elements (Fig. 5.18) are linked together to form a chain like structure which is continuously moved in one direction around running wheels of which one is motive and the other is idle. It enters one side of the combustion chamber, where it receives the fuels, it runs inside the combustion chamber carrying the fuel bed until it reaches the far end where ashes are

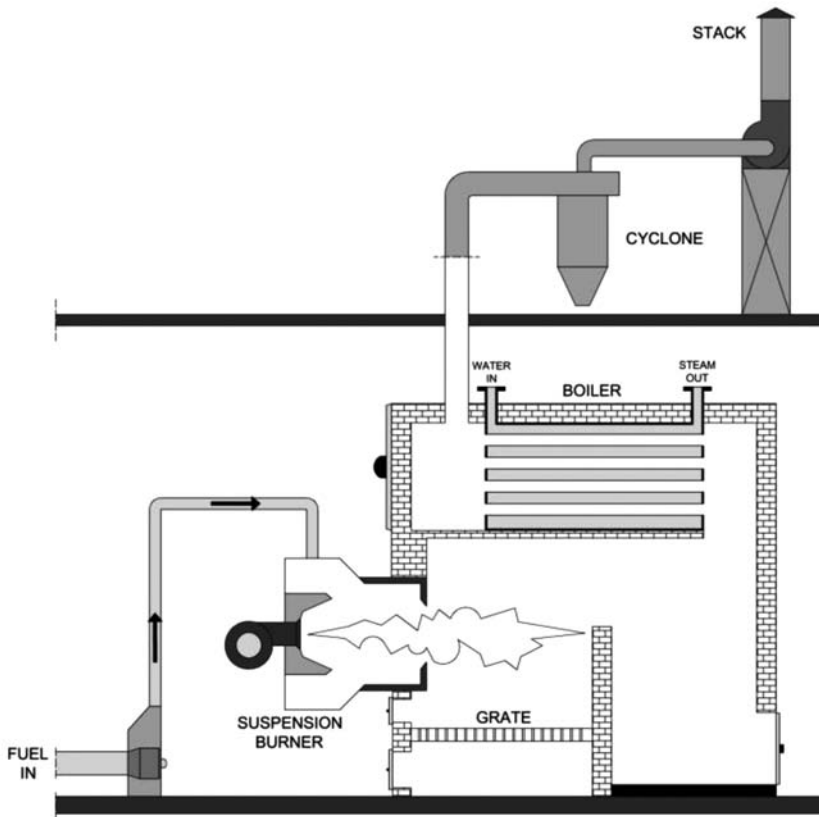


Figure 5.19. Working principle of a suspension burner with auxiliary pilot flame.

discarded and eventually it exits the chamber to reenter from the other side, after traveling the whole distance below and outside the combustion chamber. A proper grate tension is essential to guarantee the proper functioning, among the different solutions a movable shaft of the idle wheel and the free hanging of the return side of the grate to form a catenary are used.

5.3.3 Moving bed combustors

While in fixed bed combustion the solid fuel is either burnt on a pile or on a grate and there is minimal relative motion between the fuel bed and the surface on which it is laying, in moving bed combustors fuel particles are suspended in a turbulent flow of air therefore even the presence of a fuel bed may be questioned. In moving bed combustors small particle size becomes essential to guarantee the suspension, and therefore the functioning of the burner, while in fixed beds small particle size may lead to unburned particles in the flue gas and consequent fouling and particulate emissions. Moving bed combustors are divided in two categories: suspension burners, where only fuel particles are present in the air stream, and fluidized bed burners, where hot inert sand is also suspended in the air stream, to increase the heat transfer to the fuel particles.

5.3.3.1 Suspension burners

In suspension burners (Fig. 5.19) biomass fine and dry particles are blown inside the combustion chamber in a high turbulent motion by a stream of preheated primary air and are burnt before

the air stream leaves the furnace. To guarantee complete combustion a massive fuel pretreatment is necessary and particle size and humidity usually do not exceed respectively 15% and 0.6 cm, therefore for economic reasons usually they are limited to ready-to-use biomass by-products such as wood dust, rice husk etc. Some burners would require an auxiliary oil or gas pilot burner to maintain combustion, especially if the radiation from the refractory lining is not adequate to maintain the necessary temperature.

5.3.3.2 *Fluidized bed combustors*

The basic principle of a fluidized bed combustor consists of distributing air homogeneously across a combustion area where a bed of fuel and inert mineral particles is fluidized, meaning that the air velocity achieves the mass suspension of the bed particles. This is accomplished by blowing air at relatively high pressure, (around 0.15 bar relative with respect to grate firing where five times lower pressures are considered) through a distribution plate on top of which the bed of fuel and inert is positioned. A fluidized bed burner is therefore a relatively high cylindrical or square sectioned vessel that hosts on the bottom part a perforated plate positioned to divide the furnace from a pressurized air-box.

The inert material, which usually represents up to 98% of the bed material, acts as a grate because it supports the fuel which floats in it while also contributing to abrasion of the fuel particles and also acting as a refractory by radiating heat and providing conduction thanks to the continuous turbulent collision with fuel particles. The high turbulence optimizes combustion hence low excess air is required (from 10 to 30%) and the mixing effect may be used to reduce emissions as formed by injecting reactants such as urea for NO_x control and limestone for acid gases abatement, directly into the bed.

The plate and holes diameter and geometry is of primary importance to achieve an efficient air distribution which will prevent short-circuiting through a portion of the bed (channeling) and avoid the ejection of the bed (plugging) for missed fluidization. Temperature control is also particularly critical to avoid ash melting and slagging within the bed which would cause the inert particles to agglomerate and the bed to collapse. Typical combustion temperatures therefore will be kept in the 650–900°C range (Oberberger, 1998).

During startup of a fluidized bed combustor air velocity increases until it reaches the terminal velocity where the aerodynamic drag force on the particles equals its buoyancy and weight. The particles within the agglomerated bed start to disengage and the bed swells, increasing its height within the reactor, accordingly the pressure drop across the bed increases until a maximum value is achieved, corresponding to the maximum bed height. Further increases in the air velocity (within a certain range) from this value, named minimum fluidization velocity, will not modify significantly either the bed height or the pressure drop across it.

A fluidized bed working slightly above the minimum fluidization velocity is called a stationary fluidized bed or Bubbling Fluidized Bed (BFB, Fig. 5.20) because the air flowing in the bed forms bubbles that are dragged by the air flow and create typical movements and ruptures of the bed surface, when they reach the top layer, that resemble a boiling liquid. The bed material is usually silica sand of about 0.5–1.0 mm in diameter; the fluidization velocity of the air varies between 1.0 and 2.0 m/s. The secondary air is introduced through several inlets in the form of groups of horizontally arranged nozzles at the beginning of the upper part of the furnace (called the freeboard). BFB furnaces are usually considered for plants with a nominal boiler capacity of over 10–20 MW_t.

If the air velocity is further increased up to 5–10 m/s, and smaller particles of sand are used (0.2–0.4 mm in diameter), a point is reached when pressure drops across the bed plunge dramatically and pneumatic transport of bed particles is achieved. This working condition is characterized by mass extraction from the bed which must be recuperated from the flue gases, through solid separation devices such as cyclones, and continuously returned to the bed. A burner working in this manner is called Circulating Fluidized Bed (CFB, Fig. 5.21).

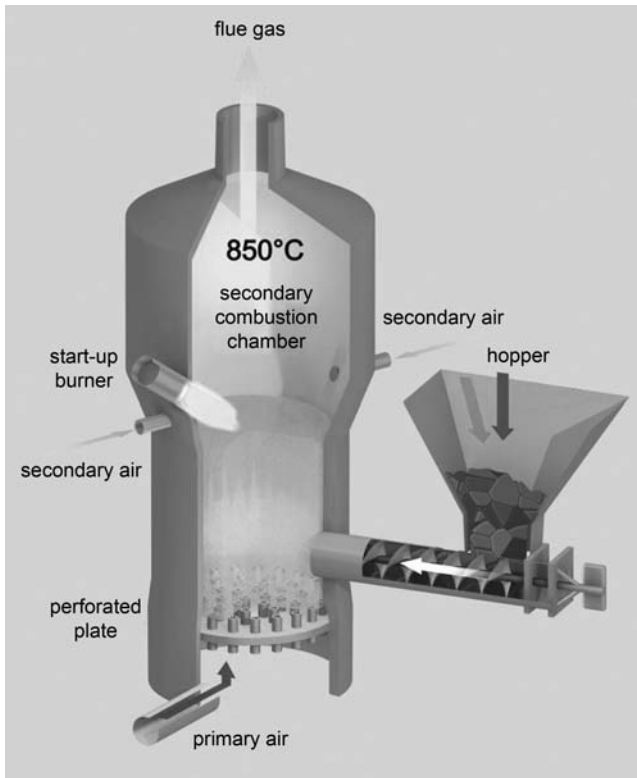


Figure 5.20. Schematic of a Bubbling Fluidized Bed (BFB).

The sand particles are carried with the flue gas, separated in a hot cyclone and fed back into the combustion chamber. The bed temperature normally is comprised between 800–900°C and it is controlled through an internal heat exchanger. The fuel amounts only to 1–2% of the bed material and the bed has to be heated before the fuel is introduced.

5.3.4 Design and operation issues

The following section provides a brief discussion of the main issues regarding the different combustion technologies that have been described previously and an insight into main design procedures for combustion chambers and some operational criticalities in terms of corrosion, slagging and fouling.

5.3.4.1 Design principles

In grate furnaces primary air passes through a biomass bed in which drying, devolatilization and char combustion take place, while secondary air to oxidize volatiles is added in a combustion zone over the bed. In the fluidized bed biomass is burned in a suspension of gas and solid bed material in which combustion air enters from below (Basu, 2006; Van Loo and Kopperjan, 2002). A comparison between grate furnaces and fluidized beds is seen in Figure 5.22.

Mass flows of air and flue gases are determined by combustion calculations. Boiler efficiency (which includes combustion efficiency) and excess air are the parameters chosen by the designer. For a biomass pile burner an efficiency ranging from 65 to 75% may be expected, while a stoker

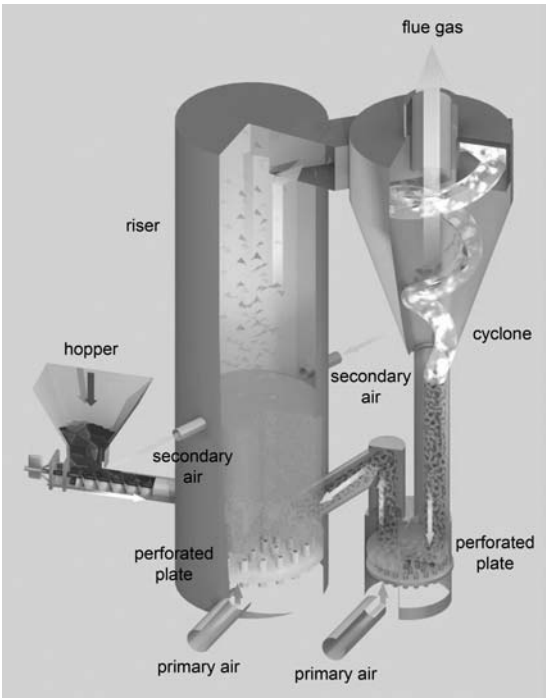


Figure 5.21. Schematic of a Circulating Fluidized Bed (CFB).

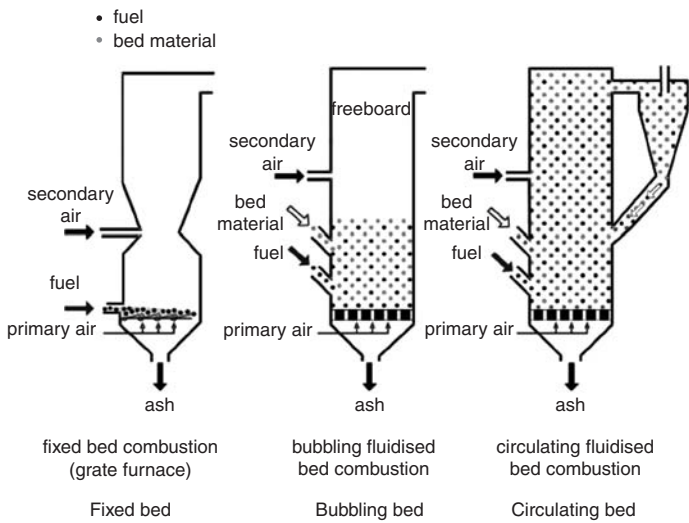


Figure 5.22. Comparison between grate furnaces and fluidized beds.

boiler an efficiency of 70 to 80% can be considered while for a biomass Fluidized Bed based boiler an efficiency ranging from 75 to 85% can be considered (US EPA, 2007). Dealing with excess air, an excess air coefficient of 40% can be considered for a bubbling fluidized bed (Basu, 2006).

Once the required power of the boiler is fixed, the amount of fuel can be determined knowing its Lower Heating Value LHV , hence assuming that the water vapors produced exit the furnace above their condensation temperature (Oka and Anthony, 2004).

$$\dot{m}_f = \frac{Q_o}{\eta_o LHV} \quad (5.29)$$

where:

- $\dot{m}_f$ = fuel mass flow [kg/s]
- Q_o = heat power output [kW]
- η_o = boiler efficiency [–]
- LHV = lower heating value [kJ/kg].

The furnace and combustion system have to be designed to optimize the following aspects: stable ignition, complete burnout; prevention of slagging and corrosion inside the furnace; prevention of fouling and corrosion on the convective heating surfaces.

The depth and breadth of the furnace must adapt to the flame form in a way that it can expand as freely as possible, also ensuring that the walls will not be touched. Beside this the design of the furnace must take into account the generation of heat (heat release) and the absorption of heat by the walls ensuring that the designed amount of fuel can be burnt in the given furnace volume, that is the fuel burnout must be completed (Baher, 1985). Besides the cross-section and height of the furnace the performance will depend on the fuel type and on the geometry and location of the heating surfaces. This means that the ash melting temperature of the fuels defines the necessary furnace outlet temperature at the furnace end before the convective heating surfaces in order to avoid sticky deposits on them (Khan *et al.*, 2009).

Dealing with heat release, each type of fuel has its specific heat release rate (Prabir *et al.*, 2000), which can be expressed in three different bases: furnace volume, furnace cross section area and water wall area in the burner region. The volumetric heat release rate is the amount of heat generated by the combustion of fuel in a unit effective volume of the furnace. It is given by:

$$q_v = \frac{B \cdot LHV}{V} \quad (5.30)$$

where:

- q_v = volumetric heat release rate [kW/m³]
- B = designed fuel consumption rate [kg/s]
- V = furnace volume [m³]
- LHV = lower heating value [kJ/kg].

A proper choice of volumetric heat release rate will ensure that fuel particles are burnt substantially and the flue gas is cooled to the required safe temperature before leaving the furnace. This temperature is known as *furnace exit gas temperature (FEGT)* and it is critical for safe operation of downstream heat exchanger surfaces.

The heat release rate per unit cross-sectional area is also indicated as grate heat release rate or grate thermal load and is given by:

$$q_F = \frac{B \cdot LHV}{F_{grate}} \quad (5.31)$$

where:

- q_F = thermal load [kW/m²]
- F = cross sectional area of the furnace grate [m²].

Typical thermal loads for coal fired furnaces are given in Table 5.8.

Table 5.8. Typical thermal loads of fixed beds combustors in coal firing (Miller, 2011).

	Heat release [kW/m ²]
Underfeed stokers	800–1500
Spreader stokers	
Stationary grates	1200–1400
Reciprocating and Vibrating grates	1800–2000
Traveling grate	2000–2200
Overfeed stokers	1200–1300

The burner zone heat release is based on water wall area in the burner region and it is defined as:

$$q_b = \frac{B \cdot LHV}{2(a + b)H_b} \quad (5.32)$$

where:

- q_b = burner zone heat release [kW/m²]
- a and b = width and depth of the furnace [m]
- H_b = distance between top edge of the uppermost burner and lower edge of the lowest burner [m].

The heat absorbed by the surrounding walls can be defined by the corrected Stefan-Boltzmann equation and thus the following equation can be written:

$$\begin{aligned} H_{\text{out}} &= \text{Heat absorbed by furnace wall} + \text{Heat carried by the gas leaving the furnace} \\ &= \frac{20.53 \cdot Fr \cdot BBSA}{m_f} [(T_e)^4 - (T_w)^4] + m_g (c_e t_e - c_a t_a) \end{aligned} \quad (5.33)$$

where:

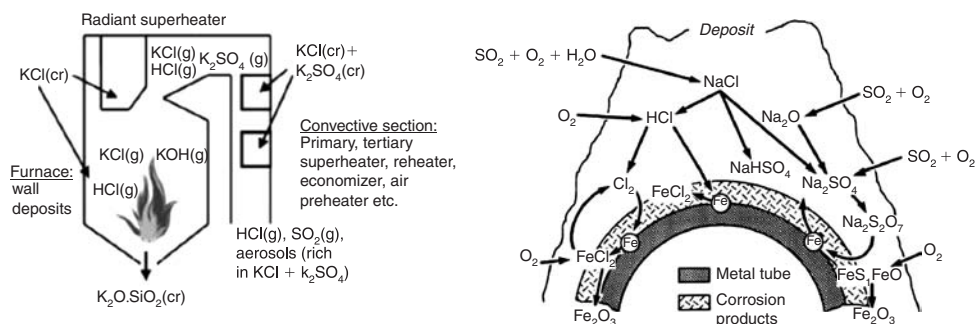
- $5.67 \cdot 10^{-8}$ = Stefan-Boltzmann constant [kJ/s m² K⁴]
- 20.53 = Stefan-Boltzmann constant [kJ/s m² K⁴]
- Fr = correction factor for geometry and emissivity [–], (0.72 for wood)
- $BBSA$ = Total effective black body surface area of the furnace [m²]
- m_f = amount of the fuel burnt [kg/s]
- T_e = absolute temperature of the exit gas [K]
- T_w = absolute temperature of the furnace walls [K]
- m_g = mass of the flue gas produced per kg fuel burnt [kg/kg]
- c_e = specific heat of the gas at temperature t [kJ/kg/°C]
- t_e = exit gas temperature [°C].

5.3.4.2 Deposit and slagging problems

Deposition (i.e. slagging and fouling) and corrosion problems are major issues in the design and operation of a combustion system. In solid fuels combustion the particulate and vapors formed during combustion can deposit on heat exchanger tubes or furnaces walls exposed to radiant heat. If the deposit is formed by molten ashes in the boiler section that is directly exposed to the flame (fire-side) the phenomenon is referred as slagging; if the deposit is formed by vapors that form a sticky layer in the convective part of the boiler the phenomenon is named fouling (Tortosa-Masiá *et al.*, 2005).

Table 5.9. Ash chemistry deposition indexes (Yin *et al.*, 2008; Juniper, 1996).

Index	Formula
Base/acid ratio	$(\text{Fe}_2\text{O} + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}) / (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2)$
Iron index	$\text{Fe}_2\text{O}_3 \times (\text{B/A})$
Slagging factor	$\text{Dry S}\% \times (\text{B/A})$
Silica ratio	$100 \text{ SiO}_2 / (\text{SiO}_2 + \text{Fe}_2\text{O} + \text{CaO} + \text{MgO})$
Critical viscosity at 1426°C	$\text{CV}_{1426^\circ\text{C}}$
Estimated ash temperature corresponding to and ash viscosity of 250 poise	$\text{T}_{250^\circ\text{C}}$
Alkali index (the ratio of the total amount of sodium and potassium expressed as their corresponding oxides to the heating value of the fuel in the unit of kg/GJ)	$(Y_{\text{K}_2\text{O}}^a + Y_{\text{Na}_2\text{O}}^a) / Q_F$
Chloride-sulfate molar ratio	$(\text{Cl} + 2\text{S}) / (\text{K} + \text{Na})$
Multi-fuel fouling index	The percentage of water-soluble alkali and alkaline-earth metals (given as oxides)
Ash melting points	Initial deformation temperature, hemispherical temperature and flow temperature

Figure 5.23. Pathways of K, S and Cl in a biomass fired boiler (left) (Khan *et al.*, 2009) and solid-phase reactions involving Cl-species in deposits (right) (Vaughan *et al.*, 1997).

Also vapors and fine particles can cause deterioration of intrinsic properties of the materials in the combustion chamber (corrosion) (Khan *et al.*, 2009) as it happens for example in straw-fired boilers. Based on fuel properties and in particular ash chemistry deposition indexes can be calculated as shown in Table 5.9.

Several experimental tests have been performed to analyze the mechanism of fly ash and deposit formation and corrosion in grate-fired boilers (Zhou *et al.*, 2007; Zbogor *et al.*, 2006; Jensen *et al.*, 1997; 2004; Michelsen *et al.*, 1998; Montgomery and Karlsson, 1999; Nielsen *et al.*, 1999; Hansen *et al.*, 2000; Montgomery *et al.*, 2002).

It has been observed that chlorine increases the volatility/mobility of alkali metals facilitating the formation of alkali silicates and alkali chlorides or hydroxides in the gas phase. When the flue gases are cooled passing the super-heater the alkali compounds condense on the heat exchanger tubes (Fig. 5.23). The initial deposit is formed by vapors and fine particles that arrive at the tube surface where alkali silicates melt at 700°C and thus provide a sticky condition on the entire surface of the tube. This sticky layer enhances further deposition of big fly ashes; this phenomenon affects only the upstream side of the tube.

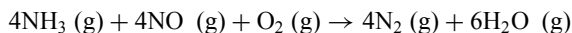
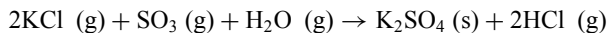
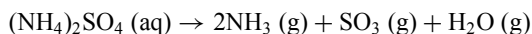
The deposits consist mainly of fly ash particles and large amounts of condensable salts, forming a matrix that glues the fly ash particles together. In the deposit the presence of KCl and K₂SO₄ with a structure of iron oxide (Fe_xO_y) has been found. A suggested corrosion mechanism for chlorine corrosion is based on gaseous Cl attack, where Fe and Cl in the metal react with gaseous Cl, forming volatile metal chlorides. This mechanism can explain the shift in corrosion behavior observed experimentally (i.e. selective corrosion is negligible at 450°C while is significant if temperature is higher than 520°C) (Yin *et al.*, 2008).

Corrosion mechanisms can be classified into three classes: corrosion associated with gas species; solid-phase corrosion and molten phase corrosion.

The same problems encountered in grate combustion can be found in fluidized bed boilers. Besides in fluidized bed reactors problems of bed agglomeration can be encountered. Agglomeration happens when a small part of the ashes remains in the bed, then ash sintering can happen through three main mechanisms: the presence of a liquid phase; solid-state sintering; and chemical reactions.

In biomass fired FBC partial melting is considered the main mechanism leading to bed agglomeration. The first mechanism is also identified as partial melting and can be further classified as highly viscous melt and low viscous melt. Highly viscous melt happens in the presence of silica this kind of melt is the most problematic because a glassy phase is produced which does not crystallize upon cooling (Llorente *et al.*, 2003; Skrifvars *et al.*, 1998). In the case of low viscous melts alkaline compounds can melt and act like a bonding agent.

Possible remedies to fouling, slagging and corrosion problems are the use of additives or co-firing with coal, peat and sludge. High temperature corrosion can be mitigated also reducing the surface temperature of superheaters. The use of additives aims to raise the melting temperatures of ashes, prevent the release of gaseous KCl and/or react with KCl to form less corrosive compounds. The materials that have been found to raise the melting temperatures of ashes include Al₂O₃, CaO, MgO, CaCO₃, MgCO₃, and kaolin (Llorente *et al.*, 2006; Van den Broek, 2000). For example the addition of 3% in weight of kaolin to chopped oats straw can raise the deformation of ashes from 700 to 1200–1280°C (Jenkins, 1994). ChlorOut (ammonium sulfate) a concept developed and patented by Vattenfall AB (Olanders and Steenari, 1995) is a very promising method. An aqueous solution of ammonium sulfate (NH₄)₂SO₄ is sprayed in the combustion zone at a temperature of 800–900°C upstream of the super heaters. It effectively converts alkali chlorides into alkali sulfates, that are much less corrosive. The spraying of ammonium sulfate can also reduce NO_x formation. The main reactions involved are:



Possible remedies against bed agglomeration for FBC systems can be: co-combustion, pre-processing of the risky fuel, use of additives and use of alternative bed materials to increase the melting point of sintering compounds. As far as additives are concerned, kaolin, dolomite, limestone, lime, alumina have been tested even if they have not been so effective. The use of alternative bed material is the most promising solution; dolomite, magnesite, ferric oxide, alumina, feldspar and aluminum rich materials have been tested (Laitinen *et al.*, 2000; Daavitsainen *et al.*, 2001; Silvennoinen, 2003).

5.4 CHEMICAL LOOPING COMBUSTION

Chemical looping is a special kind of combustion technology which is based on the splitting of global chemical reactions into two or more sub-reactions which take place in different reactors. Intermediate products are reacted and regenerated when sub-reactions occur.

Since intermediate products are produced in separate reactors, chemical looping allows separation of more easily unwanted components which are formed during the combustion process. A particular interest for this kind of combustion/separation technology is for cleaning up the flue gases from pollutants or from greenhouse gases, thus allowing having efficient and cost-effective reduced emissions combustion. Chemical looping is also interesting to split a chemical reaction with high irreversibility into more reactions which have a global lower entropy generation.

The basic feature of chemical looping is to use a medium which can participate in the reactions and facilitate the reaction of the reactants and the production of the products. Such a medium should be highly reactive at process temperature and pressure conditions and physically and chemically stable, should allow an easy separation from the reactants and the products and have moderate exothermic to endothermic heat of reactions. A medium with these features should behave as a fluid, either a liquid or a fluidized solid, being the latter more often employed.

Chemical looping combustion is a technology that can be used with any kind of fuel, either gaseous or liquid or solid, but it is more interesting with solid fuels where conventional combustion systems do not allow easy separation of intermediate products and chemical reactors are less easy to be built and operated as efficiently as for liquid and gaseous fuels.

5.4.1 Chemical looping processes

Chemical looping processes are still under development to reach full scale and commercial operation and availability. This is due to the fact that conventional processes, such as those described in the previous chapters, are efficient from an energy conversion point of view, are well known and are based on simple technical components that have been constantly improved over the centuries.

Now that the focus is shifted to environmental performance of combustion processes and greenhouse gases mitigation, the conventional technologies are showing their limits in allowing an efficient and cost effective separation of pollutants and greenhouse gases from the flue gases.

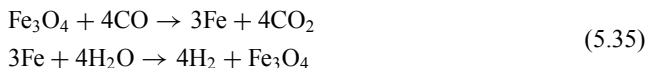
The irreversibility of the chemical reactions processes is so high that inverting the process requires a large amount of energy and complex technologies.

Most chemical looping processes currently studied and under development use a solid medium to perform the reactions.

The first chemical looping processes were developed in the early 20th century to produce hydrogen from carbonaceous fuels, using steam: the so-called steam-iron process. The global reaction is the following:



The following reactions take place in two different reactors, using as looping medium iron and iron oxide:



In the second reaction iron is oxidized by steam producing hydrogen and in the first reaction the iron oxide is reduced by CO to regenerate the oxide to Fe and produce CO₂. This process was abandoned when more efficient systems based on natural gas and oil reforming was being developed to produce hydrogen. However, a similar system was later developed to produce CO₂ from solid carbonaceous fuels. This process was based on two fluidized bed reactors using a metal oxide as medium. The process is depicted in Figure 5.24 and either iron or copper oxides may be used. The development of these early chemical looping processes to produce technical gases was prompted by the need of separating gases at a time when no other separation technologies were available.

More recently a renewed interest was raised by the need of separating gases from mixtures in much more efficient systems. In a process developed at Ohio State University (Fig. 5.25) Fe₂O₃ particles are introduced into the reducer with pulverized coal, which is gasified producing CO and H₂. Since the syngas has reducing properties, Fe₂O₃ is converted to Fe and FeO, while producing CO₂ and H₂O. Steam can be easily condensed and CO₂ can be therefore removed from the flue

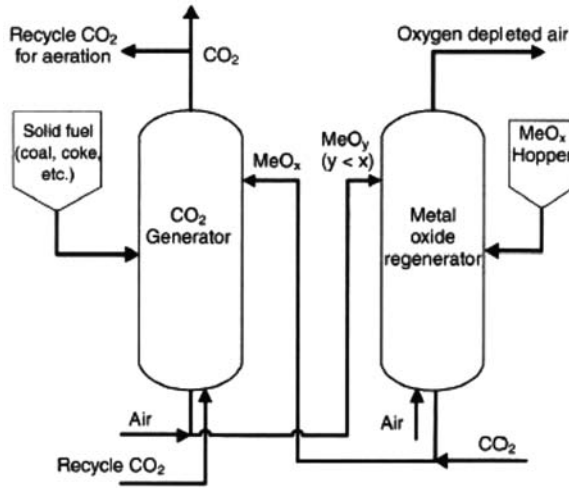


Figure 5.24. Chemical looping process for CO₂ production (Fan, 2010; Lewis and Gilliland, 1954).

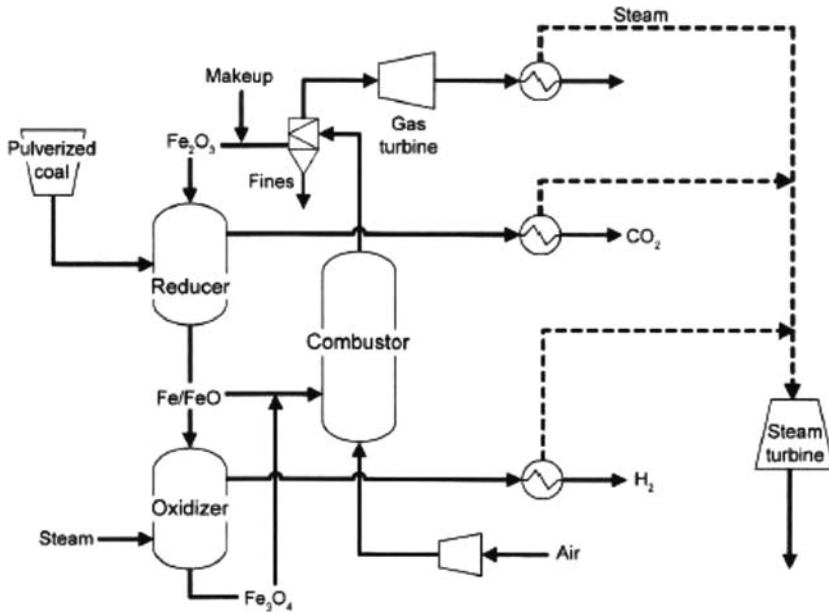


Figure 5.25. Coal-Direct Chemical Looping Process (Rizeq *et al.*, 2002; Gupta *et al.*, 2006).

gases. The Fe and FeO particles are introduced into the oxidizer where they react with steam to produce H₂ and Fe₃O₄. While being conveyed to the reducer Fe₃O₄ will be oxidized to the original Fe₂O₃.

The use of chemical looping processes is possible with any carbonaceous fuel, including biomass, and can include gasification processes in the whole power plant.

A second process which is quite interesting for hydrogen production and CO₂ separation is the HyPr-Ring Process which was developed in Japan in the 1960s and 1970s (Fig. 5.26). This process includes a gasifier, fed with coal, CaO, steam and oxygen, where the excess steam increases the

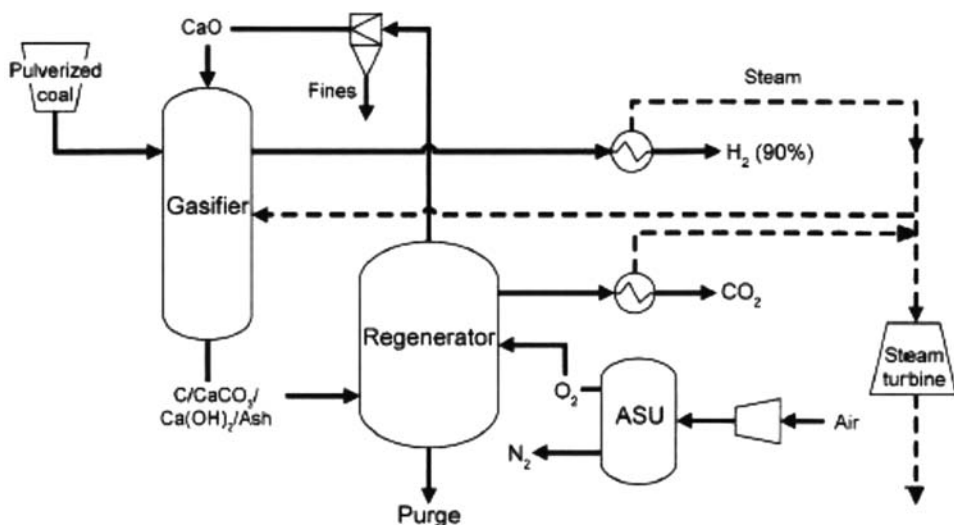


Figure 5.26. HyPr-Ring Process (Rizeq *et al.*, 2002; Lin *et al.*, 2005).

formation of H_2 , whereas CaO reacts with carbon dioxide generated in the water-gas shift reactor. The solid medium consists of $CaCO_3$ and carbon which is burnt in the regenerator calcinating the calcium components to CaO and allowing the extraction of CO_2 .

General Electric has developed a chemical looping process where coal or biomass may be used to produce hydrogen and power. The technology is quite similar to the HyPr-Ring Process, but three fluidized beds are necessary to complete the reactions. In the first reactor, coal is partially gasified with steam producing a syngas rich in H_2 , CO and CO_2 . The latter reacts with calcium sorbents. The solids in the first reactor are calcium carbonate and sulfate and unburned carbon and are introduced in the second reactor where they are reduced by Fe_2O_3 entering from the third reactor. The flue gas from the second reactor is mainly composed by CO_2 and SO_2 . The third reactor is used to regenerate the iron oxide with air. The heat of all reactors is used to generate steam and the hot air exiting the third reactor may be used in a gas turbine for power generation. In the end the GE CLC process produced power, hydrogen and allows separating CO_2 for capture or any industrial use; the scheme of this process is depicted in Figure 5.27.

Alstom has developed a combustion-gasification process based on chemical looping where three different configurations are possible: (i) coal combustion; (ii) coal gasification for syngas production and (iii) coal gasification to produce hydrogen (Fig. 5.27).

When used as a coal combustion process, the calcium sulfate is reduced to calcium sulfide, which is then burnt in the second reactor with air. Heat is transferred from the combustor to the gasifier and to a lesser extent to a steam generator to produce high temperature steam. In the second configuration more coal and more sorbents are used and hydrogen and carbon monoxide, without any CO_2 . In the third configuration, pure hydrogen is produced by adding a third reactor where a calcination reaction occurs. Calcium oxide captures CO_2 in the first reactor, separating H_2 . Calcium carbonate is calcinated by burning calcium sulfate, producing CO_2 in the third reactor. The process is shown in Figure 5.28.

5.4.2 Chemical looping reactions

In many chemical looping processes calcium sorbents are used to separate CO_2 from the other gases. These reactions generally involve absorption/calcination processes, based on the following

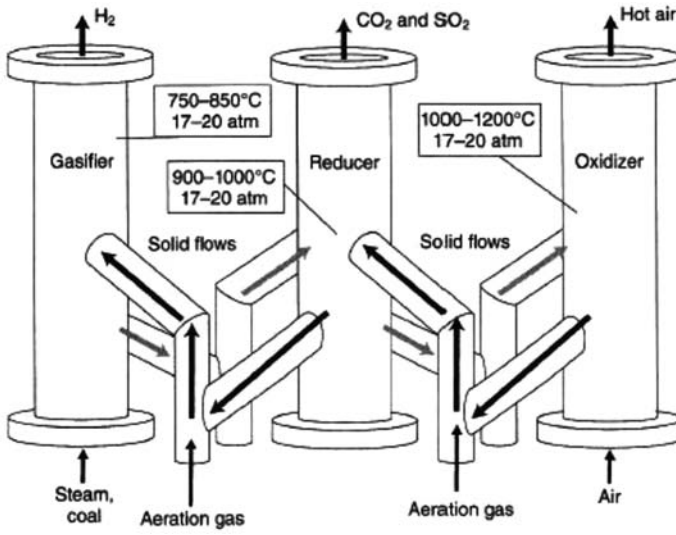


Figure 5.27. GE fuel flexible gasification system (Rizeq *et al.*, 2002; Lin *et al.*, 2005).

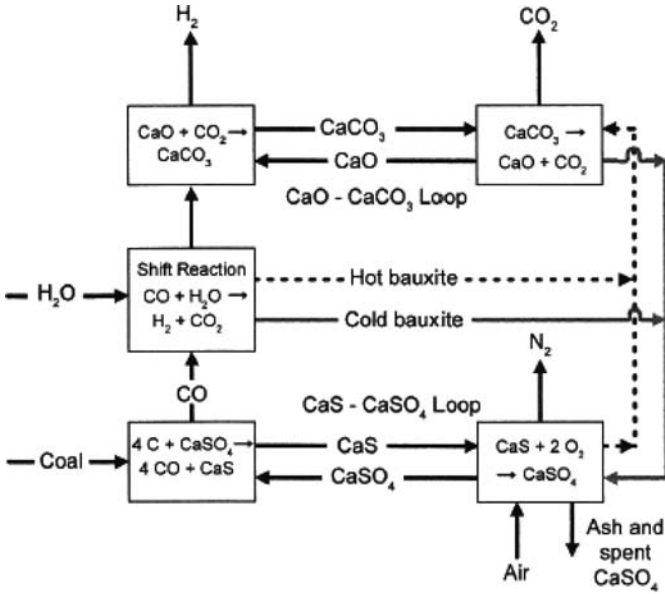


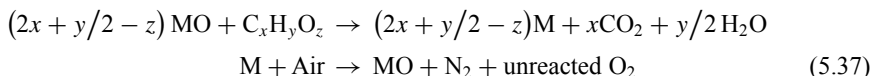
Figure 5.28. The Alstom process (Rizeq *et al.*, 2002; Andrus *et al.*, 2006).

chemical reactions:



These reactions can be shifted to the left or to the right by changing the temperature and pressure.

The combustion of carbonaceous fuels can be assumed as follows:



where the looping medium is a metal oxide. The first reaction only produces CO_2 and steam; therefore carbon dioxide may be easily separated from steam by condensing the latter. The second reactor oxidizes the metal again and the flue gases are nitrogen and oxygen. The second reaction provides heat to the first reactor. The overall combustion process is thus divided into two sub processes which separate inherently the flue gas components.

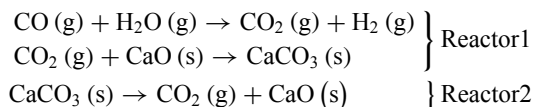
If the fuel consists of carbon only, then the chemical looping reactions can be as follows:



The looping medium is the same as in the previous reactions, but the flue gas of the second reactors is now pure hydrogen. The process allows separating CO_2 for capture and producing hydrogen as a byproduct.

The second reactor produces hydrogen instead of heat and steam is the oxidant of the overall combustion process. The carbon capture is greatly simplified and requires much less energy than in any other process producing hydrogen.

Hydrogen can also be produced including a calcination process in a chemical looping combustion:



One positive effect of capturing CO_2 in the process by means of CaO , is to enhance the hydrogen production from the first reaction because the chemical equilibrium favors its formation. The calciner in the second reactor allows an efficient separation of CO_2 from the flue gas which can be ready for capture.

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CHAPTER 6

Biomass and black liquor gasification

Klas Engvall, Truls Liliedahl & Erik Dahlquist

6.1 INTRODUCTION

Modern society is profoundly dependent on fossil feed stocks to produce multiple products, such as transportation fuels, fine chemicals, pharmaceuticals, detergents, synthetic fibers, plastics, fertilizers, lubricants, solvents, waxes, etc., as well as heat and power (Demirbas, 2006). The fossil resources are not endless. Their price is increasing continuously due to increasing scarcity, and not regarded as sustainable from an environmental point of view (Kamm, 2006). A versatile resource, especially in terms of producing carbon-based products, to replace fossil feedstocks is biomass (Vlachos, 2010) or other sources originating from biomass, such as black liquor (BL). Conversion of biomass to other products can be performed either by biochemical or thermo-chemical processes. In the case of large-scale production of, for example, carbon-based products, thermo-chemical conversion is considered more efficient compared to biochemical processes (Zhang, 2010). Techniques for thermo-chemical conversion can be divided into pyrolysis, gasification, combustion and liquefaction. Among these techniques, gasification is a versatile platform for production of multiple products, as illustrated in Figure 6.1.

Gasification has a long history starting with Thomas Shirley who experimented with “carburated hydrogen”, today called methane, in 1659 (Basu, 2010). In the beginning of the 17th century and onwards to the early 19th, gas from gasification of coal was mainly used for lightening of homes and streets and for heating. New inventions in other fields expanded the utilization of the gas in diverse applications, such as fuel for steam engines, feedstock in chemical production

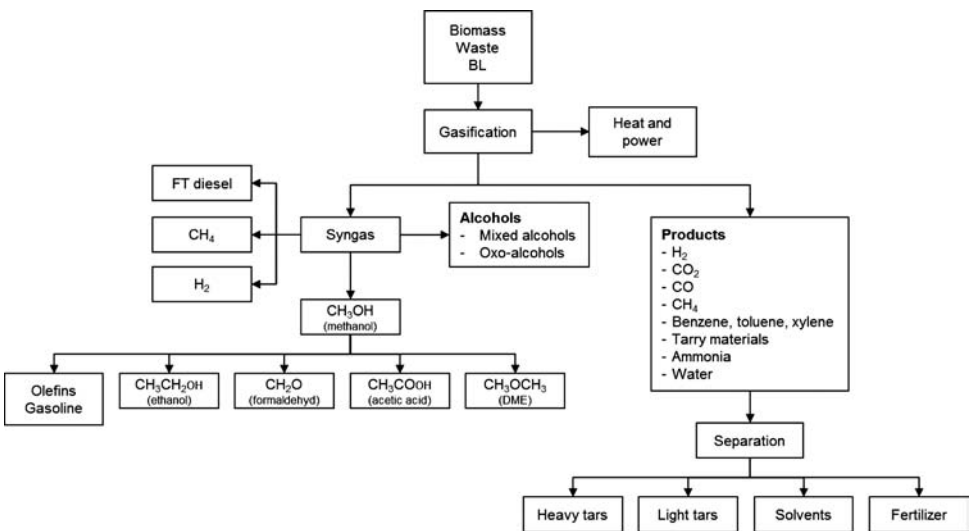


Figure 6.1. Examples of products obtained from gasification processes (modified from Demirbas, 2009).

of chemicals and motor fuels. During this time the major commercial gasification technologies, Winkler's fluidized bed gasifier in 1926, Lurgi's pressurized moving bed gasifier in 1931 and Koppers-Totzek's entrained flow gasifier were developed before the Second World War. After the Second World War the availability of abundant oil eliminated the need for gasification as a basis for production of chemicals and motor fuels. Today, the driving force for the renewed interest is the concerns about global warming and about the accessibility to fossil resources.

6.2 THEORY OF GASIFICATION

A fuel gas can be produced from biomass or other feed stocks by partial oxidation at high temperature using oxidizing agents such as air, oxygen, steam, carbon dioxide or combination of these. In case of gasification, the temperatures used are typically between 600 and 1000°C. The different steps occurring in gasification of biomass or other feedstocks are graphically represented in Figure 6.2.

The first step in the thermo-chemical conversion of a feedstock, such as biomass, is the drying of the biomass followed by the pyrolysis, of the cellulose, hemicellulose and lignin to produce char and volatiles, such as permanent gases, light hydrocarbons and tars. Introduction of reducing agents and sometimes also a catalyst further decompose the char and the tars to permanent gases. Constituents such as tars may not be completely converted and also ash from the char will be present in the formed product gas. In view of this description gasification is only one-step of many although they together generally is referred to as only gasification.

The processes graphically represented in Figure 6.3 can generally be specified in the main chemical reactions as described in reactions (6.1)–(6.6) (Engvall, 2011):

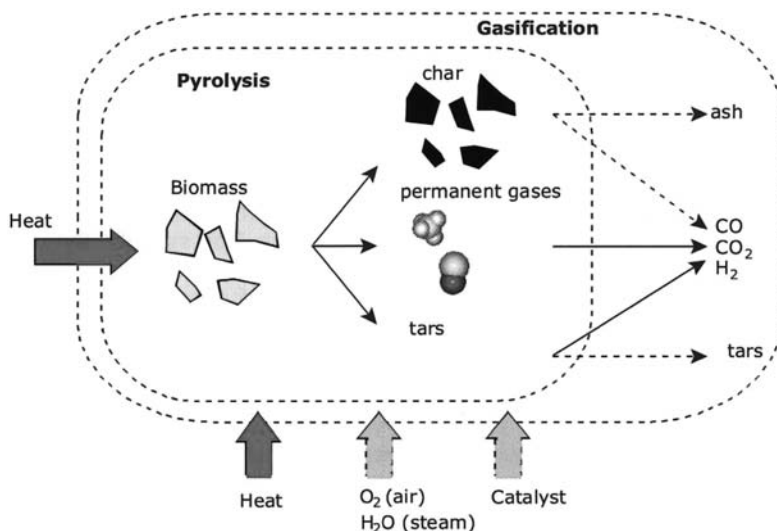
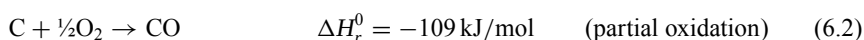
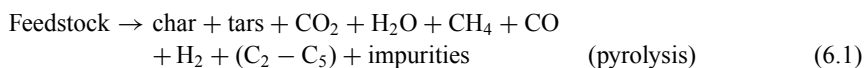
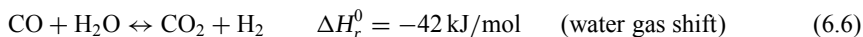
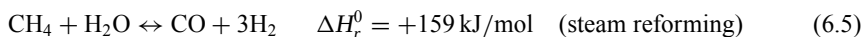
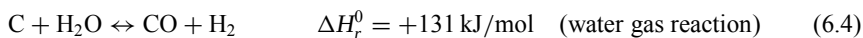
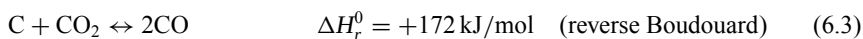
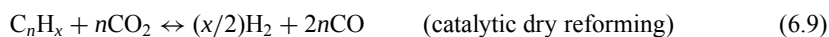
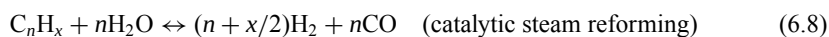
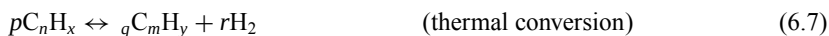


Figure 6.2. A graphic representation exemplifying the processes included in thermochemical conversion of biomass, waste or BL in a gasifier (modified from Knoef, 2005).



Reaction (6.1) describes the pyrolysis, an endothermic process, which is a very important step for biomasses due to the large fraction of volatiles (70–80% dry basis) in these feedstocks. The reactions (6.2)–(6.6) are the common reactions included in gasification of biomass. Heat for the endothermic reactions can be supplied either by direct partial oxidation directly, as e.g. described in reaction (6.2), or from an external source transferring heat to the gasifier. Other reactions that influence the product gas yield and composition are the cracking of the tars due to thermal conversion at high temperatures (reaction 6.7), or catalytic tar reforming with steam (reaction 6.8) or dry (reaction 6.9) in the presence of, for instance, a catalytically active bed material used in fluidized bed gasification:



C_nH_x represents tar, and C_mH_y represents hydrocarbon with lower carbon number than C_nH_x . The thermal conversion in reaction (6.7) is a simplification. The decomposition is generally much more complex and many different paths as proposed by Devi *et al.* (2005).

The decomposition of the feedstock is a complex process and depends on parameters, such as biomass feedstock composition, gasifying agent and the gasification process (Dayton, 2002). The gasification process produces a raw gas, generally called producer gas that consists of the permanent gases CO , CO_2 , H_2O , H_2 , CH_4 , other gaseous hydrocarbons (C_2 – C_5), char, tars, inorganic constituents and ash. The impurities in form of ash and char particulates, tar, and inorganic impurities, such as H_2S , CS_2 , COS , AsH_3 , PH_3 , HCl , NH_3 , HCN , and alkali salts, have to be removed before utilizing the gas, depending on the application of interest. Of significant importance is the tar produced, present in different amounts, depending on the gasifier technique, feedstock used and process conditions. Tar is often a confusing term because different definitions of tar are used depending on the gasifier type and the gasification operating conditions. Tar usually consists of condensable highly aromatic hydrocarbon organic compounds, ranging from molecular weight above 78 (benzene) and can generally be divided into so-called water-soluble (phenolic) and non-water-soluble (aromatic) compounds (Moersch, 2000).

The formation of tar is one of the major obstacles in the commercialization of biomass gasification technologies (Yung, 2009), causing problems in downstream process equipment, such as blocking of pipes and filters, as well as coking on catalysts in gas upgrading processes (Dayton, 2002), even at very low concentrations in the gas. Beside the tars, other impurities important to remove before utilizing the gas are generally particulates, alkali salts and sulfur-containing compounds.

In the case where black liquor is used as a fuel in the gasification, also reactions (6.10) and (6.11) take place due to the presence of high contents of alkali salts in the feedstock (Grace, 1994):



As the black liquor droplet enters the recovery unit it is exposed to hot gases and will undergo drying, pyrolysis and char conversion. The amount of salts is very high in the black liquor. This

causes some problems with respect to corrosion, but it also is acting as a very strong catalyst, and thus black liquor can be gasified at 100–200°C lower temperature than the same amount of “normal” biomass.

6.3 OPERATING CONDITIONS OF IMPORTANCE FOR THE PRODUCT COMPOSITION

This section describes some important properties of significance for the product composition after gasification.

6.3.1 *Fuel types and properties*

The performance and the selection of gasification technology are dependent on the characteristics of the fuel used. Therefore is a proper understanding of the characteristics of biomass and black liquor fuels important for a reliable selection and design of a gasifier. This chapter will briefly describe the different fuels and fuel properties of importance for gasification.

6.3.1.1 *Biomass*

Biomass is a diversified source and refers to any organic materials that are derived from plants or animals (Loppinet-Serani, 2008). Its diversity may be classified in a variety of ways depending on the origin and structure. One example is the division into two groups as proposed by Basu (2010):

- Virgin biomass, including ligno-cellulosic biomass in the form of wood, plants, and leaves; carbohydrate-based biomass such as crops and vegetables.
- Waste, including solid and liquid municipal solid waste (MSW), sewage, animal and human waste, gases derived from landfilling, as well as agricultural wastes.

Ligno-cellulosic biomass is the major source of biomass and will be briefly described below. This form of biomass can be divided into two types. Herbaceous plants are plants that have leaves and stems and die at the end of the growing season. Examples are wheat, rice, grasses, and oats. Non-herbaceous plants, which are non-seasonal remaining alive during the dormant season, including woody, plants, such as trees, shrubs and vines. Figure 6.3 shows the main components of woody biomass, consisting of extractives, cell wall components and ash. The cell wall components can in turn be divided into cellulose, lignin and hemi-cellulose. Extractives can basically be removed from the biomass by extraction with neutral solvents, including compounds, such as gums, fats, resins, sugars, oils, starches, tannins and alkaloids. The cell wall components are the polysaccharides, cellulose, linkage of glucose molecules in long chains form the structural framework of plant cell walls, and different types of hemi-celluloses, also chain-like and composed of several kinds of monosaccharides, and the complex aromatic polymer lignin. Ash is the inorganic part of the plant with the main components Si, K, Ca, S and Cl. The proportions of the main constituents are, as exemplified for wood, as follows (in percent of dry biomass): cellulose 40–45% (about the same in so-called softwoods and hardwoods); lignin 25–35% in softwoods and 17–25% in hardwoods; hemicelluloses 20% in softwoods and 15–35% in hardwoods, while the amount of extractives varies from 1 to more than 10% and ash 1–3%.

6.3.1.2 *Black liquor*

Black liquor is the residue extracted from sulfite or kraft processes after the cook in a batch or continuous digester. It contains a mixture of organics, inorganics and water. The inorganics consist of $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$, NaCl/KCl , $\text{Na K}_2\text{SO}_4/\text{K}_2\text{SO}_4$, and some residual NaOH/KOH , NaHS/KHS and non-process elements like silica, phosphate and metal ions. The organics consist mostly of lignins, but also some hemicellulose and a little cellulose. Due to the composition of the organics

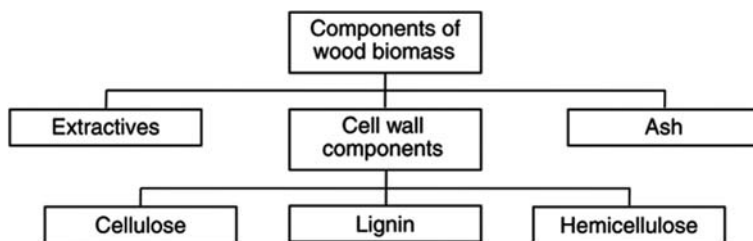


Figure 6.3. A general sketch of the components present in woody biomass (Basu, 2010).

some liquors are swelling rapidly when heated, while others do not. Because of this, different liquors can behave quite differently when gasified. The water content can vary from 50% moisture down to close to 0% moisture if dried in a last step of processing, but the moisture content (MC) typically is 20–30%.

6.3.1.3 Biomass properties of importance for gasification

The important properties of biomass of significance for gasification can roughly be divided as follows:

- Physical and thermodynamic properties:** The physical properties of biomass depend markedly on the type of feedstock. For instance, density may vary from 100 kg/m³, for balsa, bagasse and straw, to 1200 kg/m³, for lignum vitae (Di Blasi, 1997). Permeability to gas flow and thermal conductivity not only vary with the biomass species, but also along, across and tangentially to the wood fiber-chains. Furthermore, the effective physical properties of char probably reflect those of the virgin biomass and thus show significant variation with the feedstock. All cereal straws resist compaction, which make them difficult to compress for economical transport and storage. Processed biofuels do generally have a higher calorific value than the raw material itself, caused by the disposal of the moisture content and air in the structures of the biomass during processing. Since gasification is a thermochemical conversion process the thermodynamic properties of a biomass plays a significant role in the gasification process. Biomass, as such, is highly anisotropic with different thermal conductivity along the fiber compared to across the fiber bundles. The conductivity also depends on factors such as moisture content, porosity and the present temperature. An example of the thermal conductivity dependency on the dry density along and across the grain is shown in Figure 6.4. Other important properties are the specific heat, depending on the moisture content and the actual temperature, and the ignition temperature. The ignition temperature is the temperature where the thermochemical process becomes self-sustainable and is generally lower for biomass fuels with a higher volatile matter content. However, it also depends on the surrounding conditions such as oxygen partial pressure, particle size and heating rate.
- Chemical composition and energy content:** All organic compounds in lignocelluloses contain oxygen, but the degree of oxidation varies, so that the polysaccharides contain more oxygen than lignin and the extractives. The quantities of cellulose, hemicellulose and lignin vary between different types of biomass plants. Each of these components has their own pyrolysis chemistry in thermo-chemical conversion, and therefore the composition of the volatilized intermediary compounds can vary substantially depending on biomass used and (Mohan, 2006) and hence also influence the composition after gasification. The energy content varies between different biomass fuels as exemplified by straw, refused derived fuel (RDF) and municipal solid waste (MSW), algae and non-organic residue with low heating values (LHV) of 18.0, 22.9, 23.1 and 33.0 MJ/kg, respectively (Phyllis, 2012).

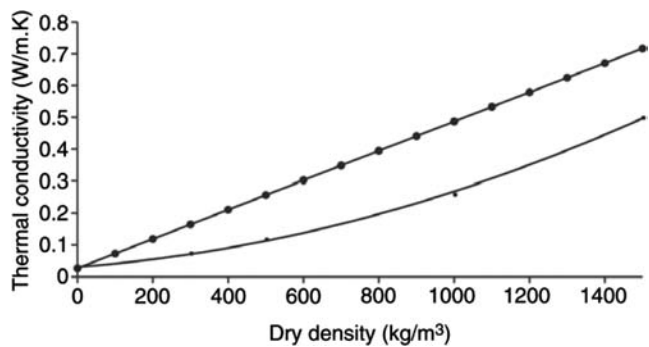


Figure 6.4. Thermal conductivity dependency on the dry density along and across the grain. Straight line is along the fibers and the curved is across the fibers (Basu, 2010).

Table 6.1. Typical gas compositions using air or oxygen/steam as gasifying agents.

Product gas composition	Oxygen/steam (Nossin, 2009)	Air (Knoef, 2005) Atmospheric RDF ¹⁾ (Vol.%)
	Pressure = 22 bar Wood chips (Vol.%)	
H ₂	14.8	8.6
CO ₂	8.4	15.6
CO	20.3	8.8
CH ₄	8.9	6.5
H ₂ O	47	9.5
N ₂	–	45.8
C _x H _y	na	4.9

na = not analyzed.

¹⁾Refuse-derived-fuel.

6.3.2 Gasifying agent

The gasification process requires the addition of an oxidizing or gasifying agent, such as air, oxygen, steam, carbon dioxide or combination of these. Depending on gasifying agent used, different calorific values of the product gas will be obtained (Wang, 2008). For example, if steam is used as the gasifying agent, the heating values of the product gas are typically 10–15 MJ/m³N and in case of air typically 3–6 MJ/m³N (Wang, 2008) for gasification of biomass. Typical gas compositions using air and oxygen/steam as gasifying agents in fluidized bed gasification are shown in Table 6.1.

Two parameters used to describe the measures of the air or oxygen flowrate is the equivalence ratio (*ER*) and the superficial velocity (*SV*). *ER* and *SV* are defined as the ratio of airflow to the airflow required for stoichiometric combustion of the biomass, which indicates the extent of partial combustion, and as the ratio of air flow to the cross-sectional area of the gasifier, which removes the influence of gasifier dimension by normalization, respectively (Yamazaki, 2005). Therefore, both the *ER* and the *SV* are directly proportional to the airflow. In case of using air as the gasifying agent, the air supplies with oxygen for the combustion process and by varying the air flow, in for example fluidized bed gasification; it will influence the degree of combustion, which also affects the gasification temperature. A higher airflow rate, results in a higher temperature, resulting in a higher biomass conversion. This is true as long as oxygen is not supplied in excess causing a too high degree of combustion of the biomass, resulting in decreased energy content of the product gas. If a too high air flow is used, the residence time will be shorter, which may

reduce the extent of biomass conversion. Other factors of importance for the effect of *ER* on the product gas are e.g. temperature and steam to biomass ratio.

Steam as a gasifying agent increases the partial pressure of H_2O in the gasifier. This favors the water gas reaction (eq. 6.4) as well as water gas shift (eq. 6.6) and methane reforming reactions (eq. 6.5), where the latter two occur at gasification temperatures above $750\text{--}800^\circ\text{C}$ (Kumar, 2009; Turn, 2010; Lucas, 2004). The addition of steam results in an increased amount of H_2 in the product gas. The temperature of steam is generally lower than the gasification temperature and therefore a large amount of heat is needed to elevate the steam temperature and thereby maybe lowering the temperature in the gasifier. This need more pronounced above a certain steam-to-biomass ratio where the product gas will be affected negatively. It is therefore recommended to preheat the steam or any gasifying agent before introducing it into the gasifier, to induce a higher gasification temperature.

6.3.3 Temperature

The temperature is one of the most important gasification parameter influencing the product gas composition in the gasification process. A higher temperature will result in higher conversion efficiency and thereby increase the product gas yield and in a decrease in tar content (Kumar, 2009; Narváez, 1996). The contents of H_2 , CO , CO_2 and CH_4 are affected due to a simultaneous interplay of the reactions (6.3) to (6.6), when the temperature is increased. At temperatures above $750\text{--}800^\circ\text{C}$, the H_2 and the CH_4 content will increase and decrease, respectively, as a result of the endothermic nature of the H_2 production reactions (6.4), the water gas reaction and (6.5), the steam reforming as well as a reverse of the exothermic water gas shift reaction (6.6). If the temperature is further increased to temperatures above $850\text{--}900^\circ\text{C}$, also the reverse Boudouard reaction (6.3) plays a substantial role together with the reactions (6.4) and (6.5).

6.4 GASIFICATION SYSTEMS

Flexible utilization of biomass or black liquor to useful products by means of gasification is carried out in more or less complex systems, including beside the gasifier a variety of upstream and downstream process components selected depending on the requirement of the application and also use of fuel. Examples of components in gasification systems are illustrated in Figure 6.5.

In the subsequent sections below different gasification as well as downstream process technologies are briefly described.

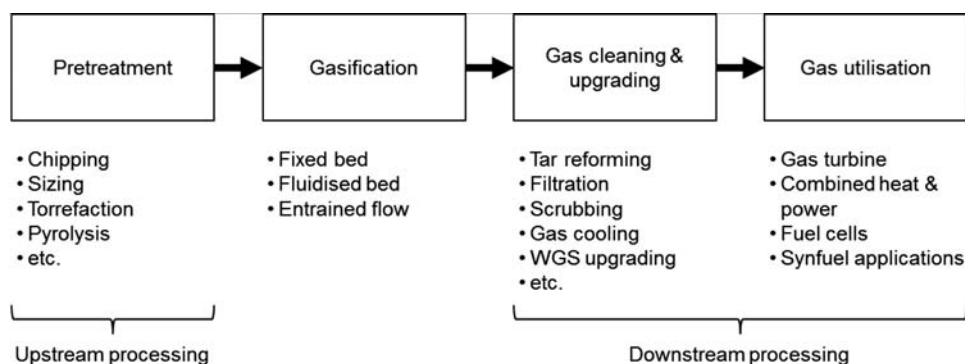


Figure 6.5. Different steps included in a gasification system.

Table 6.2. Comparison of the three fixed bed gasifier technologies (adapted from Knoef, 2005).

Fuel (wood)	Updraft	Downdraft	Crossdraft
Moisture wet basis [%]	<60	<25	10–20
Dry-ash basis [%]	<25	<6	0.5–1.0
Ash melting temperature [°C]	>1000	>1250	
Fuel size [mm]	5–100	20–100	5–20
Application range [MW]	2–30	1–2	
Gas exit temperature [°C]	200–400	700	1250
Tar [g/Nm ³]	30–150	4.5–5.0	4.0–4.5
Gas LHV [MJ/m ³ N]	5–6	85–90	75–90
Hot-gas efficiency [%]	90–95	3–4	2–3

6.4.1 Gasification technologies

The reactor types suitable for biomass gasification can be simply categorized into fixed beds and fluidized beds according to the relative motion between solid and gas and the bulk density of the solid-phase in the reactor. The principal types of gasifiers are: downdraft or co-current fixed beds, updraft or counter-current fixed beds, cross-draft fixed bed, bubbling fluidized beds and fast or circulating fluidized beds. Additional types include the entrained bed and the fluidized bed twin-reactor concept (Bridgwater, 1995). In general one gasifier technology is not appropriate for the full range of applications, i.e. there is a suitable range of applications for each gasifier technology. In the case of the fluidized bed technology and the entrained flow, the range is >10 MW and >100 MW, respectively.

6.4.1.1 Fixed bed

In a fixed bed gasifier, the fuel is supported on a grate where the fuel moves down in the reactor as a plug. This type of gasifier is generally suitable for small-scale operation in the range of 10 kW–10 MW. In Table 6.2 the three main types of fixed bed technologies are compared.

6.4.1.1.1 Updraft gasifiers

The fixed bed updraft gasifier has been the principal gasifier of use for coal for about 150 years. A schematic of an updraft gasifier is shown in Figure 6.6a. In this gasification concept, the biomass is fed into the top of the reactor, and the air or oxygen into the lower zone. The fuel (and the resulting char) flows slowly down and passes sequentially through drying, pyrolysis, gasification and combustion zones by gravity. In parallel is the pyrolysis vapors carried upward by the up-flowing hot product gas. Ashes are removed by an ash discharge system at the bottom of the gasifier.

In the lower gasification zone, the solid char from pyrolysis and tar cracking is partially oxidized by the incoming air or oxygen. Steam may also be added to provide a higher level of hydrogen in the gas. The sensible heat of the product gas is recovered by direct heat exchange with the entering fuel feed, which thus is dried, preheated and pyrolyzed before entering the gasifier. The product gas temperatures are relatively low, 300–600°C, since the heat is used for preheating, drying and pyrolysis of the incoming fuel.

The tars in the pyrolysis vapor will either condense on the cool descending fuel particles or be carried out of the reactor with the product gas, thus contributing to its high tar content. The extent of this tar bypassing may be up to 20% of the pyrolysis products. The condensed tars are recycled back to the reaction zones, where they are further cracked to gas and char. The product gas from an updraft gasifier contains a significant proportion of tars and hydrocarbons, and these contribute to the relatively high heating value of the gas. The product gas requires substantial clean-up if further processing of the product gas is to be performed.

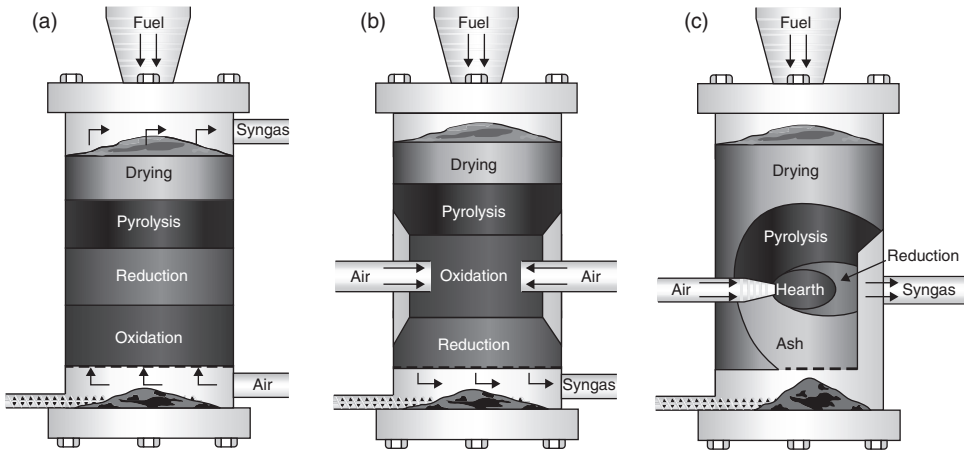


Figure 6.6. Schematics of three different fixed bed gasifiers: (a) updraft, (b) downdraft and (c) cross-draft (Olofsson, 2005).

The dust content of the gas is, however, relatively low because of the filtering effect of the drying and pyrolysis zones and the moderate gas velocities.

Updraft gasifiers can handle fuels with moisture contents up to 60 wt% and particle sizes between 5 and 100 mm, thus covering a wide span of fuels and fuel sizes. In principle there is no upper limitation with respect to size, this in contrast to the downdraft gasifier. The principal advantages of updraft gasifiers are their simple construction and high thermal efficiency.

6.4.1.1.2 Downdraft gasifiers

The downdraft gasifier was originally developed for gasifying high volatile fuels, for example wood and biomass. The reactor is schematically shown in Figure 6.6b. The fuel enters the gasifier at the top of the reactor and its main feature is the concurrent flow of gases through a slowly downwards descending packed bed of solids.

The bed is supported by a constriction in the middle section known as the throat, where most of the gasification reactions occur. It is in this section that the air or steam/oxygen is added. The reaction products are intimately mixed in the turbulent high-temperature region around the throat. Most of the tar cracking takes place in this high-temperature region. Some tar cracking also occurs below the throat on the residual charcoal bed, where the gasification process is completed. In order to minimize radial temperature gradients, it is of importance that the oxidizing agent is distributed homogeneously throughout the whole cross-section of the throat. In the bottom, there is a system to recover the ash and other non-volatile components.

Fixed bed downdraft gasification is relatively simple, reliable and proven and it results in a high conversion of the pyrolysis intermediates and hence giving a relatively clean gas. It is suitable for dry fuels (up to 25 wt% moisture), blocks or lumps with a low ash content (<6 wt%) and containing a low proportion of fine and coarse particles, preferably between 10 and 300 mm (in the longest dimension). Owing to the low content of tars in the gas, this configuration is generally favored for small-scale electricity generation with an internal combustion (IC) engine. The physical limitations of the throat diameter and particle size relation result in that there is a practical upper limit to the capacity of this configuration of about 500 kg/h or 500 kW_e. The temperature of the gas is approximately 700°C.

6.4.1.1.3 Cross-draft gasifiers

A cross-draft fixed bed gasifier variant of a so-called co-current fixed bed gasifier where the fuel is fed from the top and the air from the side. The difference from the downdraft version is the product gas outlet on the side opposite of the air inlet. A schematic is shown in Figure 6.6.

The air is introduced in the reactor at high velocity creating a hot zone, also called the hearth, with a temperature above 1500°C due to combustion of part of the char. The remaining char is gasified to CO in the subsequent zone. The heat from the combustion is conducted to the pyrolysis zone where the fresh biomass is pyrolyzed when passing. The cross-draft is generally used for small-scale units and allows for a simple reactor construction due to the small combustion zone and the insulating effect of the fuel and the ash. Due to the high temperature, the concentration of tar in the product gas is low, as shown in Table 6.2, and therefore a fairly simple gas cleaning system can be used after the reactor.

6.4.1.2 Fluidized bed gasifiers

The basis for the fluidized bed reactor configurations is the principle of fluidization. By forcing a gas stream (fluidization medium) through a reactor, the fuel together with the inert bed material will behave like a fluid, if the flow velocity is high enough. Air, steam or steam/oxygen mixtures are examples of commonly used fluidization media. Silica sand is the most extensively used bed material, but other bulk solids, especially those exhibiting a catalytic activity, such as olivine sand and dolomite, are also employed.

Fluidized beds provide many features not available in the fixed-bed types, including high rates of heat and mass transfer and good mixing of the solid-phase, which means that reaction rates are high and the temperature is more or less constant in the bed.

Depending on the velocity of the fluidization medium, the fluidized bed gasifiers may be divided into two categories, bubbling fluidized bed (BFB) gasifiers and circulating fluidized bed (CFB) gasifiers.

6.4.1.2.1 BFB and CFB reactors

The bubbling fluidized beds operate at relatively low gas velocities, typically below 1 m/s. In the BFB gasifier most of the conversion of the feedstock to product gas takes place in the dense bed region in the bottom of the gasifier, even though some conversion continues in the freeboard section owing to reactions associated with entrained (small) particles. Because of the relatively low gas velocities in the BFB gasifier, freeboard gasifier elutriation is minimal and the addition of new bed material limited. A schematic of a BFB gasifier is shown in Figure 6.7a. The circulating fluidized beds, illustrated in Figure 6.7b, operate at much higher gas velocities, 3–10 m/s, and are significantly different in their hydrodynamics, compared to a BFB reactor. The solids are dispersed all over the tall riser, allowing for a long residence time for both the gas and the fine particles. In the CFBG, the particles are separated from the gas in a cyclone and recycled back to the bottom of the reactor. For fly ash/ dust removal are in both configurations a particle filter employed.

The inert bed material will enhance the heat exchange between the fuel particles, and therefore the fluidized beds will operate under almost isothermal conditions. For both configurations, the maximum operating temperature is limited by the ash-induced melting point of the bed material that typically will lie between 800 and 900°C. At these relatively low temperatures, coupled with the prevailing relatively short gas residence times, will the (slow), especially heterogeneous, gasification reactions normally not reach chemical equilibrium. This is especially true for the faster CFB gasifier. Thus, for example, methane concentrations tend to be much higher than those suggested by the chemical equilibrium. Additionally, tar levels are normally between those of the downdraft and the updraft fixed bed gasifiers.

The conversion of the feedstock is high in a fluidized bed gasifier, almost 100%. This only, however, if the carryover of fines is limited, which predominantly may occur in top-feeding configurations.

Due to the geometry and the excellent mixing properties, fluidized beds may be scaled up with confidence. However, fuel distribution may become problematic in large beds, although multiple feeding can solve the problem partly. The energy throughput per unit of reactor cross-sectional area is higher for a CFB gasifier than for the BFB gasifier. Both configurations can be operated under pressurized conditions, which will further increase the energy throughput. Pressurized conditions are also beneficial if the eventual subsequent downstream upgrading calls

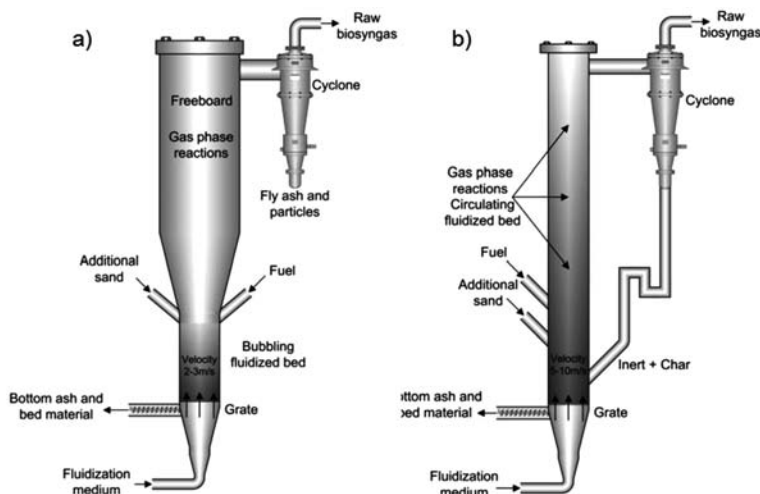


Figure 6.7. Schematics of fluidized bed gasifiers: (a) bubbling fluidized and (b) circulating fluidized bed (Olofsson, 2005).

for pressurized conditions, as for instance the Fischer-Tropsch synthesis. The intense mixing allows the reactor to perform well over a broader fuel particle size distribution, starting already with relatively fine particles. Furthermore, in contrast to other reactor systems, the fluidized bed gasification allows for the possibility to use additives, e.g., for *in-situ* removal of pollutants (like sulfur) or primary measures to increase tar conversion via employment of catalytically active bed materials. Alternatively, a subsequent catalytic or thermal reactor can be added.

Loss of fluidization in fluidized beds due to bed sintering is one commonly encountered problem, depending on the thermal characteristics of the ash. Alkali compounds from the biomass ash form low-melting eutectics with the silica sand, which is the usual bed material. This may result in agglomeration and bed sintering, resulting in eventual defluidization and subsequent shutdown of the gasifier. The presence of chlorine will amplify this problematic effect, as often alkali and chlorine go together. By applying proper counter measures, such as adding additives with alkali-attracting properties may part of this problem be handled though. With biomass of high ash/alkali content, it may be advisable to use alternative bed materials such as alumina or magnesite. The main drawback with these more sophisticated bed materials is that of cost.

The CFB can run with most kinds of fuels, from coal to waste, including biomass. For larger CFB gasifiers, it is often preferable to employ a few smaller cyclones in parallel in contrast to only one large cyclone.

6.4.1.2.2 Dual fluidized bed reactors

One of the major problems in air gasification is the dilution of the product gas by the nitrogen in the air. This could be overcome by using oxygen as the gasifying agent. However, the use of oxygen requires an oxygen generator and is expensive and highly energy extensive. Another route to achieve a product gas without diluting nitrogen is to separate the combustion process from the gasification process in two reactors in a so-called dual fluidized bed configuration.

A typical dual bed fluidized bed gasifier is made up of two reactor chambers, the gasifier and the so-called riser combustor. An example of this configuration is shown in Figure 6.8, where the fast internal circulating fluidized bed (FICCFB) gasifier, developed by Vienna University of Technology in Austria, is illustrated. The system combines a bubbling fluidized bed gasifier with a circulating fluidized bed combustor, where the gasifier in effect is a pyrolysis, indirectly heated with hot sand from the riser, which in turn is heated by burning the product char with air before

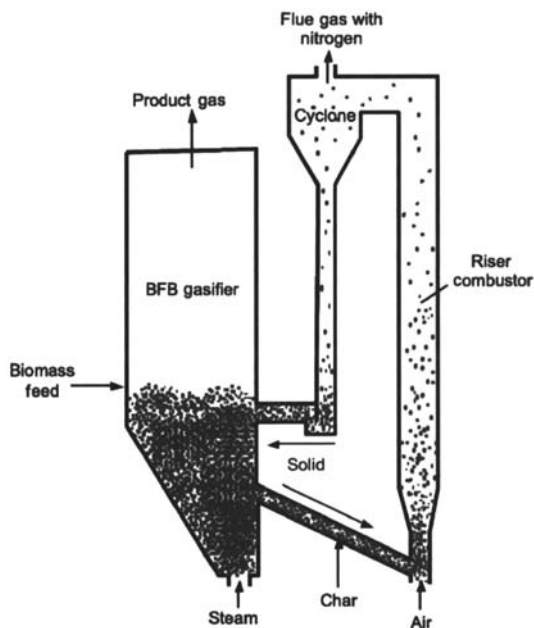


Figure 6.8. A twin bed gasifier process two circulating fluidized bed reactors (Basu, 2010).

re-circulation back to the gasifier. Steam is also usually added for enhancing hydrogen generation *via* the shift reaction and to promote the carbon-steam reactions. Product quality is good from a heating value perspective, but poor in terms of the tar content. These gasification configurations normally give middle-caloric gas with the heating value (*LHV*) of 10–14 MJ/m³N as the resulting gas will be almost nitrogen-free.

Another concept with a combination of a gasifier and a combustor is the SilvaGas (Batelle) process shown in Figure 6.9 has been tested in several countries. The idea is that fuel is heated with solids from the combustor, and char is fed to the combustor after the gasification to get good conversion efficiency. The gasifier can in this case be operated with steam and by this achieve a richer gas.

6.4.1.3 Entrained flow gasifier

The entrained flow reactor (EFR) is well-known in coal combustion processes whilst the experience with biomass is limited. In entrained flow gasifiers, no inert material is present but a finely ground feedstock is required. The fuel particles are fed co-currently with the oxidant agent and subsequently are the particles entrained with the gas stream. The EFR gasifiers operate at temperatures of 1200–1500°C, depending on whether air or oxygen is employed. Examples of entrained bed gasifiers are seen in Figure 6.10.

The temperatures in the EFR gasifiers are much higher than those encountered in fluidized bed gasifiers; hence, the product gas does contain low concentrations of tars and condensable gases. The high temperatures allow for the thermal conversion of tar and also some of the methane, thus the composition of the product gas will be close to those indicated by the chemical equilibrium. This even though the residence times are very short only around 1 second.

The conversion in the entrained beds configurations effectively approaches 100% and exhibit, in theory, the highest capacity of all gasifiers. However, the high-temperature operation creates problems of construction materials selection and ash melting.

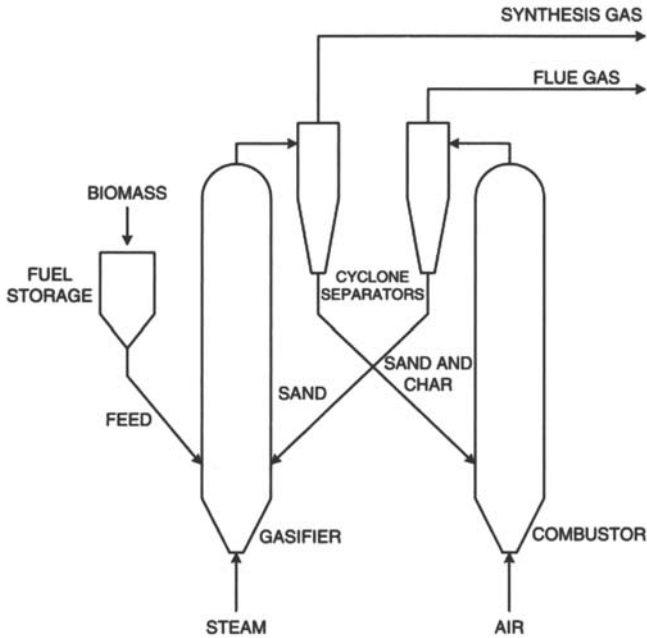


Figure 6.9. A twin bed gasifier process based on two circulating fluidized bed reactors (Paisly, 2002).

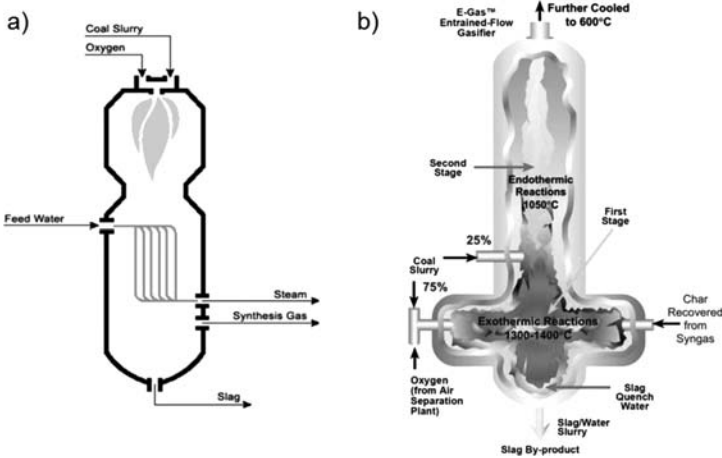


Figure 6.10. Two examples of entrained flow gasifiers: (a) downflow and (b) upflow (Olofsson, 2005).

After the fuel pre-treatment the feedstock enters the gasifier as a pulverized solid by a pneumatic feeding. The mixing between the fuel and the oxygen should be as good as possible in order to optimize the gasification. Depending on the type of fuel, soot may also be formed. To avoid the soot formation, addition of steam in a proportion of 0.1 kg steam per kg oxygen is often necessary. When coal is used as a fuel it is crushed into a fine powder ($\sim 50 \mu\text{m}$). This touches upon the main disadvantage with respect to biomass application, as fine milling of biomass is very costly. This drawback can be partially handled by pre-treating the biomass through e.g. torrefaction.

However, this is at present a relatively unproven technology. In addition, in order to reach these high temperatures more product gas has to be combusted, which will hamper overall efficiency and thus costs. Another possibility is to pyrolyze the biomass to pyrolysis oil to be able to feed the oil into the reactor. This is possible if the pyrolysis oil is directly introduced in the gasifier and not stored since the oxygen-rich pyrolysis most likely will polymerize when stored. The polymerized pyrolysis oil forms two phases where the most energy-rich phase is very viscous and not possible to pump.

Entrained flow gasifiers may be found as slagging and non-slagging. In the slagging entrained flow gasifier configuration, melted slag products, originating from the fuel, are condensed, usually on the reactor wall, as it is the coldest part of the gasifier. The melt will accumulate on the wall, forming a slag layer that protects the wall from the high temperature corrosive atmosphere of the gas. The liquid slag is removed from the bottom of the gasifier. In order to get a liquid slag with the right viscosity at the given temperature, so-called fluxing material must usually be added. In coal-based power plants, limestone or other Ca-rich materials are often added into the bed.

The non-slagging entrained flow gasifiers do not produce any slag due to small amounts of minerals/ashes in the fuel. A small amount of soot is often deliberately generated in order to get condensation surfaces in the gas bulk by nucleation to preventing fouling of the walls by the slag.

Entrained flow gasifiers may also be used for gasifying black liquor. An example is the operation at SCA Ortviken in Sweden with recovery of liquors from a Ca-sulfite plant during 1970 and 1986. The reactor had injection of black liquor together with oil in the upper center and air was introduced around it. The residence time was very low, just a few seconds, and the temperature around 725°C. The gas was cooled in a waste heat boiler and solids separated in a Venturi scrubber. Since black liquor consists of large amount of alkalis severe materials problem is to be expected at high temperature. At SCA Ortviken, the material problems were handled in the reactor and proved that at least 725°C was practical for long-term operations using Högånäs bricks as insulation inside the reactor.

6.4.2 Gas cleaning and upgrading

The gases formed by gasification are more or less contaminated depending on the process and the feedstock. Depending on the gas utilization, some kind of gas cleaning must thus be applied to prevent eventual problems in downstream process equipment such as plugging, erosion, corrosion, and catalyst poisoning, but also to prevent pollution of the environment. Table 6.3 shows the main requirements for a general syngas.

The product gas from biomass gasification will contain fine carbon-containing ash particles, which are difficult to remove only by cyclones. Barrier filtration methods using e.g. sintered metal or ceramic filters are therefore employed. The differential pressure over the filter tends to increase as deposits build up over time. Problems with filter clogging by soot resulting from the thermal cracking of tars both in the gas phase and on the filter surface. This problem can partly be handled by cooling the gas to <500°C and lowering of the gas velocities through the filter.

Table 6.3. Purification level of main syngas impurities (Boerrigter, 2005).

Impurity	Removal level
Sum of sulfur compounds ($\text{H}_2\text{S} + \text{COS} + \text{CS}_2$)	< 1 ppmV
Sum of nitrogen compounds ($\text{NH}_3 + \text{HCN}$)	< 1 ppmV
$\text{HCl} + \text{HBr} + \text{HF}$	< 10 ppbV
Alkaline metals	< 10 ppbV
Solids (soot, dust and ash)	Essentially completely
Organic compounds (hydrocarbons, tars)	Below dewpoint

However, temperatures should not be allowed to fall below 400°C due to the potential problem of tar condensation and subsequent clogging.

Hot gas cleanup is to be preferred if the sensible heat of the gas has to be retained and thus are low temperature scrubbing systems for tar removal often avoided.

Tar concentrations in the gas are mainly a function of the gasification temperature, the higher the temperature the lower the tar concentration. Tar levels and tar characteristics are not only a function of temperature though, but also of the feedstock, gasifier configuration and processing conditions. The tars formed in pyrolysis are thermally cracked in most environments to refractory tars, soot and gases. However, the problems associated with tar during gasification of biomass differ from those when gasifying coal or peat and thus are the methods for tar handling developed for coal gasification not directly transferable to biomass gasification applications.

6.4.2.1 Tar and tar removal

Tars in the product gas can be tolerated if the gas is to be used as a fuel and closely coupled to the applications, such as boilers and kilns. For these applications, cooling and condensation of the tars can be avoided, and the energy content of the tars adds to the calorific value of the product gas. However, in more demanding applications tars in the raw product gases, even at low concentrations, can create major handling and disposal problems. Different systems for tar removal are shown in Figure 6.11. As soon as the temperature of the producer gas drops below the dew point, tars will either form aerosols or directly condense on the inner surfaces of the equipment, resulting in plugging and fouling of pipes, tubes, and other components downstream from the gasifier.

Aerosols are especially difficult to remove by filtration or scrubbing systems, causing deposits in the cooler parts. At temperatures above about 400°C , tars can also undergo subsequent dehydration reactions to form solid char and coke that further tend to plug up systems. The most important consideration is often to maintain the producer gas above the tar dew point ($\sim 400^{\circ}\text{C}$), thus avoiding condensation in the pipes. Internal combustion engines and methanol synthesis

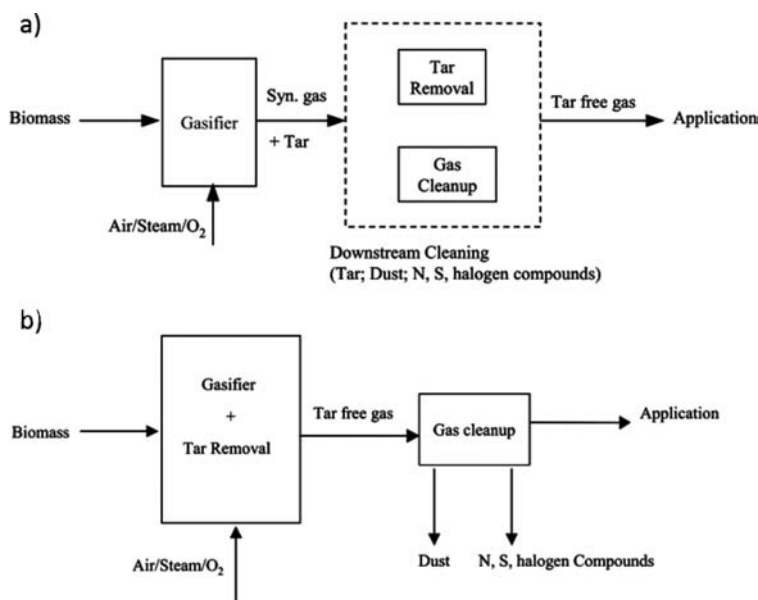


Figure 6.11. Different tar removal concepts: (a) secondary methods and (b) primary methods (Devi, 2003).

applications require that the gas be cooled before final use. However, there are many technical and economic reasons, such as thermal efficiency, environmental emissions compliance and tar-effluent treatment costs, to justify catalytic cracking and reforming of tars before cooling.

IC (internal combustion) applications require that particles and tars be lowered to about 30 mg/m³N for particulates and 100 mg/m³N for tars. Ideally, gas turbine applications require that the hot gas is completely cleaned and remains hot (and under pressure) before use. It is not practical, or thermodynamically efficient, to cool down the gas after gas generation in the gasifier. The range of the particulate concentration limit for gas turbines is 0.1 to 120 mg/m³N, depending on the design and the operating conditions. Alkalis are also critical contaminants, and the reduction of these to acceptable levels (usually below 0.1 mg/m³N) remains a great challenge.

Hydrocarbons also possess potential problems for the methanol synthesis processes. To prevent catalyst poisoning (particularly the copper/zinc-based catalysts), total olefin content should be less than 6 mg/m³N and the ethene concentration should be below 4 mg/m³N. The catalysts are also very intolerant to the presence of sulfur and chlorine, as will be discussed.

Two basic approaches may be identified to remove tars from product gas streams:

- The physical methods are utilized for removing condensed tar aerosols, using technologies similar to those used for particulate removal such as wet scrubbers, electrostatic precipitators, or other technologies. These require that the product gas be cooled to ensure the tars are in a condensed form.
- The catalytic and thermal tar reduction methods have been studied to convert the tars to permanent gases. The catalytic approaches can potentially destroy tars in either the vaporized or the condensed state. These two approaches are discussed more in below, and special emphasis will be put on the catalytic tar cracking techniques as these possess the most promising techniques for tar removal.

In these techniques for physical tar removal, tars are removed from the gas stream by cooling the product gas, allowing tar condensation into aerosol droplets. Thereafter, the droplets are removed by systems similar to those used for particulate removal. The two most common techniques for this are wet scrubbing and electrostatic precipitation. As a result of the physical tar removal, a condensate contaminated with tars is generated and this condensate has to be treated.

In the wet scrubbers tars are collected by impinging the material on water droplets. Those tar-containing water droplets lead to a decanter where the bulk tars are separated from the aqueous phase. The use of water in these scrubbers needs the gas temperature at the exit to be in the range of 35–60°C (Stevens, 2001). Generally, particulates and other gas impurities, such as acidic or alkaline compounds, are removed simultaneously with tars by these techniques. It is possible that the condensation of tars on particulate surfaces can lead to plugging and fouling of gas conditioning equipment. Nevertheless, the use of wet scrubbers for small applications has proven to be a less reliable method for tar elimination because of their cost.

Tar removal in the electrostatic precipitators is based on the same principles as particulate removal. The collector surfaces of the electrostatic precipitators are washed continuously to remove the tar material. These collectors can operate up to about 150°C, but preferably at lower temperatures to avoid tar vaporization. The electrostatic precipitators are efficient removing tars and particulates from the product gas stream as they can remove up to 99% of particles less than ~0.1 µm. However, the use of these systems in large-scale biomass gasifiers is rare because of their high operating and investment costs.

In the wet scrubbers and wet electrostatic precipitators, tars are collected as a tar-water mixture. The biomass tars include a wide variety of organic compounds, and most of them are at least to some extent water-soluble. This implies that, the wet waste cannot be clearly separated into organic and aqueous fractions. An incomplete separation of the effluent into two phases can be accomplished by settling though, but the resulting organic product still contains large amounts of water (typically 50%wt or more). The separated aqueous phase also contains lower molecular weight oxygenates including organic acids, aldehydes, and phenols. Plain wastewater cleanup and

tar disposal is not feasible due to environmental concerns. Treatments for the aqueous wastewater are commercially available, but will increase costs. The most common techniques employed are: adsorption of dissolved organics by carbon, wet oxidation of wastewaters, and dilution and biological treatment of wastewaters. The operational costs of these wastewater treatments are, in principle, directly proportional to the contamination level of the condensate.

6.4.2.2 *Thermal and catalytic tar decomposition*

The methods to remove tars from product gas are in principle thermal, by for example by partial oxidation or direct thermal exposure or catalytic. In these processes, tars decompose to form additional product gas. Tar destruction can be accomplished thermally only at above about 1200°C or with catalysts at moderate temperatures of 750–900°C. These approaches have the potential to increase conversion efficiencies while simultaneously eliminate the need for collection and disposal of tars. The catalytic cracking of tars can be very effective, up to >99%.

6.4.2.2.1 *Thermal processes for tar destruction*

While catalysts facilitate tar destruction at intermediate temperatures, tars can also be cracked thermally at higher temperatures, typically above 1000°C. The minimum temperature required for efficient tar destruction is not well characterized; it depends on the types of tars formed in the gasifier. Thus, thermal destruction of the oxygenated tars from updraft gasifiers might be treated at lower temperatures than the refractory ones from high temperature reactors. Apart from economical and material problems, thermal decomposition at high temperatures can lead to soot formation, which can be even more troublesome than the aromatics. The difficulties of achieving complete thermal cracking, in parallel with operational and economic considerations, often make thermal cracking less attractive in large-scale gasification systems.

6.4.2.2.2 *Catalytic processes for tar destruction*

This approach has the potential advantage that tars can be rapidly destroyed as they are formed or just thereafter, eliminating downstream problems. The tars are cracked to smaller molecules on the catalyst surface, and the mechanisms of tar destruction are reasonably well documented. The ideal catalyst may be characterized as follows: effective in the removal of tars, resistant to deactivation, easily regenerated, strong and inexpensive. Additionally, they may be capable of reforming methane thus providing a suitable syngas ratio (if the desired product is syngas) (Sutton, 2001).

Tar decomposition catalysts used in biomass conversion can be divided into two different types depending where in process the catalyst performs; primary and secondary catalysts. The primary catalysts are added directly into the biomass prior to gasification whilst the secondary catalysts are placed in a secondary reactor downstream from the gasifier.

The primary catalysts are added directly to the biomass prior to its gasification. The addition can be done either by wet impregnation of the biomass material or by dry mixing of the catalyst. These catalysts may catalyze the gasification reactions, but their main purpose is to reduce the tar content of the product gas. They operate at the same conditions as the gasifier, they are usually non-renewable and consist of low-cost disposable materials. Normally, they have little effect on the methane and C2–3 hydrocarbon conversion. It has been noticed that the primary catalyst alternative tend to be more problematic with respect catalyst deactivation, erosion and elutriation. Therefore, more emphasis has been put on studying and investigating the separate secondary catalytic bed alternatives.

The secondary catalysts are placed in a secondary reactor downstream the gasifier. Since the catalytic bed operates independently of the gasifier, these catalysts can operate under different process conditions than those of the gasification unit. This type of catalyst is also active in hydrocarbon reforming and often in methane reforming.

Additional advantages with this alternative are that the pyrolysis reactions do not continue in the catalytic reactor and that it is easier to arrange for a good catalyst-gas contact in a separate catalytic reactor. Particles and other impurities may also be removed before catalyst exposure

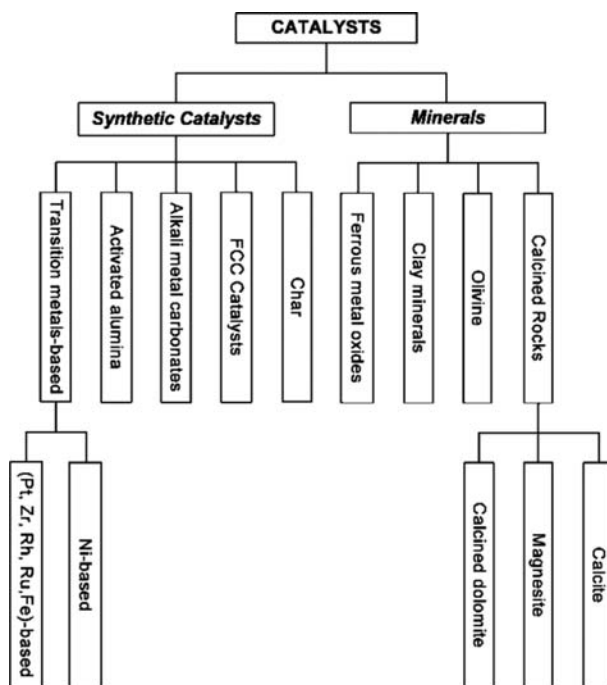


Figure 6.12. Classification of different catalyst materials for tar cracking (Abu El-Rub, 2004).

and the temperature and other process conditions in the catalyst reactor may as mentioned, be controlled separately from those of the gasifier.

Several different materials have been investigated and classified as potential catalyst. Figure 6.12 illustrates the different types of catalytic materials (Abu El-Rub, 2004). The catalytic materials most comprehensively studied are dolomites, both as primary and secondary catalysts, nickel-based, mainly as secondary catalyst and alkali metals, mainly as primary catalyst.

6.4.2.2.3 Dolomite catalysts

The use of dolomite as a catalyst in biomass gasification has attracted much attention because it is a low cost material that significantly can reduce the tar content of the product gas from a gasifier. With suitable ratios of biomass to oxidant agent, almost 100% elimination of tars can be achieved. Dolomite is a magnesium-calcium ore with the general formula $\text{MgCO}_3 \cdot \text{CaCO}_3$ that contain additional minerals at trace levels, such as SiO_2 , Fe_2O_3 and Al_2O_3 . The chemical composition of dolomite, as well as many of its characteristics, such as surface area and pore diameter, varies from source to source. Dolomites are the most active with the calcination reaction ($\text{MgCO}_3 \cdot \text{CaCO}_3 = \text{MgO} \cdot \text{CaO} + 2\text{CO}_2$). The activity can be directly related to the surface area, pore size and pore distribution. A higher activity has also been observed when iron oxide is present.

Dolomites are generally used in a secondary bed downstream from the gasifier, but they can be used as a primary catalyst, dry-mixed with the biomass. Claimed dolomites can be placed in the gasifier with good result, but they tend to be brittle and thus erode easily.

Dolomite decomposes in principle all tar compounds but naphthalene, thus naphthalene has been identified as the most abundant condensable compound after reforming of tars over dolomite at 800–900°C. This point to a limitation of the dolomites as catalysts if the overall aim is the total elimination of all tars from the product gas. The naphthalene conversion varies with the steam partial pressure, reaching a maximum for a steam concentration of 5–15% and overall naphthalene conversions have been reported to be 80–95% with dolomite (Sutton, 2001).

An additional drawback with dolomite is its eventual use at pressurized conditions. This because dolomite must be calcined for performing acceptably and calcined dolomites can be re-carbonated depending on the temperature and partial pressure of the carbon dioxide. For example, at 900°C, CaO will be carbonated to CaCO₃ if the partial pressure of carbon dioxide exceeds 100 kPa. Thus, the use of dolomites as catalysts are, in principle, restricted to biomass gasification applications at atmospheric pressure.

Deactivation due to carbon deposition has been also reported. Nevertheless, the relatively high amounts of steam used in gasification can be effective in maintaining the activity of the dolomite catalysts. The catalyst is also sensitive towards chlorine in the gas phase since it easily forms CaCl₂ at the actual temperature present in the gasifier or the tar cracking reactor (Nemanova, 2011). CaCl₂ has a relatively low melting point at 782°C, which is lower than the temperature normally used in the gasifier or a cracking reactor, > 800°C. The CaCl₂ will form a soft outer layer at the bed particles. This layer will be more easily abraded and will also cause a blocking of the pore structure, i.e. the material will be completely non-active in terms of catalytic activity.

6.4.2.2.4 Nickel catalysts

Most of the available literature on catalytic gas cleaning for biomass gasification involves nickel catalysts. The nickel catalysts are typically supported on materials such as α -alumina, magnesia, magnesium aluminum spinel and calcined zirconia. They perform best as secondary catalysts located in a separate reactor downstream, which can be operated under different conditions than those of the gasifier. Tar contents of 4 mg/m³N and less have been reported (Aznar, 1993). The Ni-based catalysts designed for steam reforming of heavy hydrocarbons seems to be active for tar removal (Arauz, 1997).

In principle no tar is formed as long as the Ni-catalyst is active, deactivation is due to sulfur poisoning, carbon fouling and (thermal) sintering of the nickel particles. The problem with sulfur poisoning increases with pressure and secondary Ni-based fixed beds tends to deactivate easier than the secondary fluidized ones.

Carbon deposition, and hence, catalyst deactivation may be reduced by introducing a guard bed of dolomite or by adding dopants to the catalyst, such as lanthanum (Sutton, 2001). By using a guard bed of dolomite, the removal of tar up to 95% can be achieved, followed by the adjustment of the gas composition and final tar cracking using a second catalytic nickel bed.

The nickel-based catalysts are commercially available and effective in the removal of hydrocarbons and adjustment of the gas composition to syngas quality. However, the nickel catalysts have potential drawbacks *vis-à-vis* cost, intolerance to oxygen breakthrough and disposal.

6.4.2.2.5 Alkali metal catalysts

Alkali metal catalysts for product gas tar reduction have also been studied. However, most of the work carried out in this field focuses on the effect of the catalysts on the gasification and pyrolysis reactions. The alkali metal catalysts are often used as primary catalysts, added directly to the biomass by dry mixing or wet impregnation. When directly added to the gasifier bed, these catalysts tend to increase the rate of gasification, reduce the tar content (sometimes significantly) and reduce the methane content of the product gas (Sutton, 2001). However, they tend also to be rapidly deactivated and the recovery of the catalysts is difficult and costly.

Inherent in the ash of several biomass types are the high concentrations of alkali and these ashes are effective catalysts for tar decomposition (Hauserman, 1994).

Alkali metal catalysts are also active as secondary catalysts. For example, potassium carbonate supported on alumina is more resistant to carbon deposition than nickel, although it is not as active.

6.4.2.3 Removal of other impurities found in the product gas

6.4.2.3.1 Alkali metal compounds

Alkali metal compounds may be found in the vapor phase at high temperatures and will therefore pass through particulate removal devices unless the gas is cooled. The maximum temperature considered to be effective for condensing alkali metal species is around 600°C. Tests have shown

that their gaseous concentrations fall with temperature so much that the concentrations are close to turbine specifications at temperatures 500–600°C. Thus, gas cooling down to these temperatures may result in condensation of the alkali metals on the entrained solids and thus be removed with the overall particulate removal.

Alkali metal vapors may damage ceramic filters at high temperatures, and the gas thus has to be cooled before passing through the hot gas filter. Alkali metals may cause high-temperature corrosion of turbine blades, stripping off their protective oxide layer and for this reason, it is believed that the alkali concentration should not exceed 0.1 ppm at entry to the turbine. There is no experience with modern coated blades in such an environment. Alternatively, or additionally, water scrubbing can be employed for alkali removal.

6.4.2.3.2 Fuel-bound nitrogen

Most of the fuel-bound nitrogen is normally converted to mainly ammonia and smaller quantities of other gaseous organic nitrogen containing compounds (50–80%) during gasification of biomass. These compounds are all in the vapor phase and will therefore pass through all particulate removal devices and they will cause potential emissions problems by forming NO_x , during subsequent combustion.

There are in principle four options of approaching the problem of nitrogen oxide emissions. These may be used singly or in combination:

- Reduction of the formation of NO_x , by limiting fuel-bound nitrogen in the feedstock through careful selection of biomass types and/or blending.
- Wet scrubbing, which will remove ammonia and other soluble nitrogen compounds, but results in loss of sensible heat and thus hamper efficiencies.
- Use of selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) downstream the subsequent combustion. Both these methods involve a reaction between ammonia and NO , to form nitrogen and water. These are well-established technologies and they are often used for NO_x -reduction. However, there is a cost and an efficiency penalty.
- Use of sophisticated gasification techniques for minimizing the conversion of fuel-bound nitrogen to ammonia and subsequent use of alternative sophisticated combustion techniques for enhancing the *in-situ* SNCR reactions.

6.4.2.3.3 Sulfur

The sulfur content of biomass is relatively low, 100–200 ppm. Thus the product gas will contain about the same amount of sulfur, primarily as hydrogen sulfide. These levels are not problematic from an environmental viewpoint, but for processes involving subsequent catalytic upgrading must they be reduced by up to 90%. This because sulfur readily forms metal sulfides, which makes it an often encountered catalyst poison, even at (very) low sulfur concentrations. This property also makes metals or metal oxides suitable for sulfur purification or sulfur adsorption. However, a suitable candidate for sulfur capture should preferably be relatively easy to regenerate, a property that often is difficult to combine with that of good sulfur adsorption properties. The most often employed sulfur purification methods are the “wet” methods, which call for relatively low temperatures. In flue gas, cleaning is this normally not problematic as an efficient combustion process call for relatively low flue gas temperatures. However, during gasification, with subsequent catalytic upgrading, is it preferable not to lower the temperature before the upgrading for reasons of energy efficiency. Thus are high temperature dry desulfurization methods to prefer, but these are yet to be fully developed.

6.4.2.3.4 Chlorine

Chlorine is another potential contaminant, which may originate from pesticides and herbicides as well as in waste materials containing, for example PVC. A level of 1 ppm is often quoted, but this is a function of the temperature, chlorine species and co-contaminants, etc. Chlorine tends to form low melting salts with nickel and calcium (dolomite) with may hamper the subsequent

catalytic tar cracking or catalytic reformation and upgrading of the product gas. Chlorine can be removed by absorption in active material either in the gasifier, in a secondary reactor or through wet processes.

6.5 GASIFICATION APPLICATIONS

There is a large number of different gasification techniques, developed and under development, to select from when planning for a gasification based conversion processes. Each technique has there advantages and disadvantages depending on factors such as:

- The scale of the conversion process considered. For example, large-scale production of transportation fuels or chemicals, pressurized gasification systems are economically more feasible (Hamelinck, 2004).
- The biomass feedstock that will be used. Here we also have the question of the availability of the feedstock as well as the needed feedstock flexibility of the gasifier.
- The requirements from the application, such as power generation with gas turbine, FT-diesel or methanation, concerning the quality of the synthesis gas or product gas.

There are also other factors that may influence the choice of gasification technology.

R&D activities in the area gasification of biomass to commercialize the technology started already in the 1970s and since then several projects to demonstrate the technology have been executed. So far, due to economic and political incentives, there are no advanced large-scale plants, such as IGCC for heat and power as well as syngas production, in operation today. In the sections below a few selected examples of recent ongoing activities within the field is presented.

6.5.1 Biomass gasification

6.5.1.1 BFB gasifier at Skive

Carbona has developed the atmospheric BFB gasification process for a CHP plant in Skive, Denmark, for biomass gasification, based on the licenses from the Gas Technology Institute (GTI), their own R&D work, as well as in conjunction with Vattenfalls project VEGA. Figure 6.13

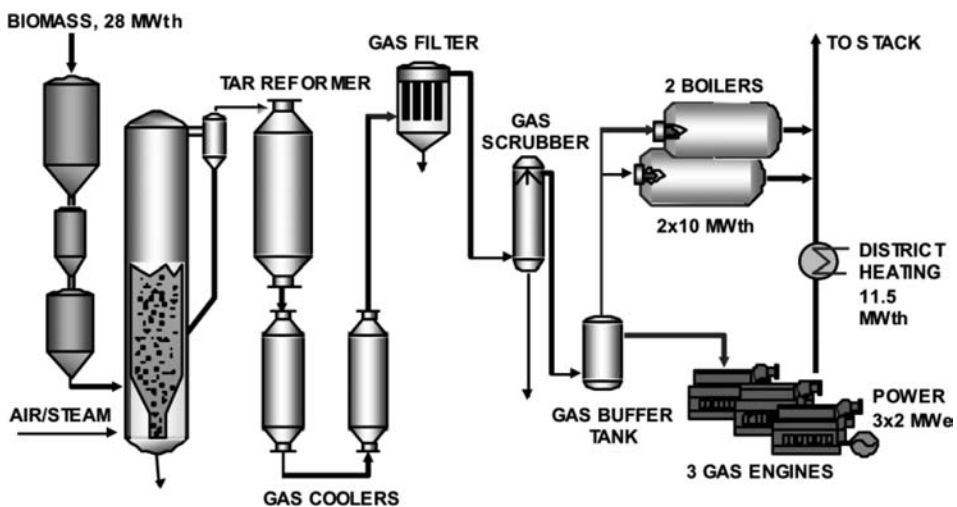


Figure 6.13. Simplified scheme of the Andritz Carbona Low-Pressure Bubbling Fluidized Bed gasification process.

illustrates the gasification process, including also the flow diagram of the gas engine based CHP plant. The maximum power and district heat generation is 5.5 and 11.5 (95/50°C), respectively. The gasifier with a fuel capacity of 28 MW_{fuel} is basically a cylindrical steel vessel with a layer refractory lining equipped with a cyclone to return eventual entrained ash, bed material or char to the gasifier. The gasifier is fed with 110 tpd of wood pellets biomass by using through live bottom-type hoppers of special design and metered by a screw conveyer system. The fluidizing gasifying media is air, in the low pressure cases gas, introduced into the reactor through a special gas distributor. In principle, oxygen and steam could also be used. Secondary air may be introduced into the freeboard to control the temperature and enhance tar cracking. The cross section area of the fluidized bed is sized to maintain the fluidization velocity at the full and part load operating conditions of the gasifier. The freeboard cross-section area is larger than the bed area to decrease gas velocity to reduce the entrainment of particles thereby increasing the solids and gas residence time. The fluidized bed consists of inert material in form of dolomite to provide the primary bulk of the bed for heat transfer purposes, but also to act as a catalyst for tar reduction.

The produced product gas consists primarily of H₂, CO, CO₂, CH₄, lower hydrocarbons, water vapor, N₂ and some tars. One of the advantages, claimed by Carbona, is that the gasifier design produces a product gas with relatively low quantity of tars, due to the vigorous mixing in the bed, the use of active dolomite as bed material, large feedstock particle size as well as a relatively low gas velocity, which gives a higher residence time for tar in the gasifier. In addition, the use of secondary air in the freeboard contributes to the reduction of tars.

The BFB gasifier is claimed as having a simpler construction compared to a gasifier based on CFB technique. The reason for this is the lower gas velocity, causing smaller amount of fines elutriated from the bed to be circulated, minimizing the size and also the wear of the recycle cyclone. The low amount of entrained fine materials also enables introduction of a secondary catalytic tar-cracking step directly after the gasifier, and thus a cooling and filtration step is avoided before the tar-reforming step as is the normal case for e.g. CFB based processes.

The Skive plant is equipped downstream with gas cleaning in form of a catalytic tar reformer where the catalyst material could be either Ca or Ni based. After the gas cooling to approx. 200°C, the product gas is cleaned of particulate matter in a fabric filter. Downstream of the filter the fuel gas is further cooled and cleaned in a gas scrubber close to ambient temperature and used in three gas engines or in two boilers.

The project to build the plant was financed on a commercial basis, but as it is a demonstration facility; the EU, the US Department of Energy, and the Danish Energy Agency provided subsidies. The plant was commissioning started in late 2007 and, using one gas engine, operations began in the summer of 2008. The second and third gas engines were installed in 2008 and are now all in operation.

6.5.1.2 Cortus WoodRoll gasification technology

Cortus AB, funded in 2006, is developing a new-patented biomass gasification process WoodRoll®, which is based on a three-stage indirect gasification technology with a separation of the drying, pyrolysis and gasification. The process is illustrated in Figure 6.14.

The steps of the process (Fig. 6.14) can be described as follows:

- (1) Inside the drying reactor the moisture content of the fuel is decreased. Heat is generated in a separate hot gas generator with gas from the pyrolysis process (2).
- (2) During the pyrolysis of biomass generally three components are achieved during the decomposition; char, tar and pyrolysis gas. Heat is recovered from flue gases from the burners (5).
- (3) The pyrolysis gas produced is incinerated in the drying reactor and the gasifier.
- (4) Char is milled to a small grain size before entering the gasification reactor.
- (5) Radiation tube burners which are fired with pyrolysis gas in heating the gasification reactor.
- (6) Steam from the syngas cooler is injected.

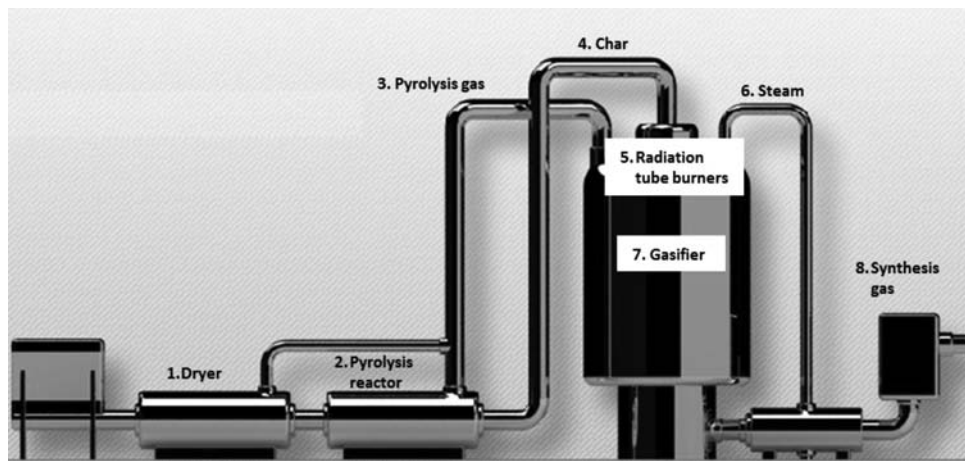


Figure 6.14. Illustration of the WoodRoll® process.

- (7) Syngas is produced from steam and char in the high temperature gasifier at a temperature of around 1100°C.
- (8) The produced gas is cooled, conditioned and compressed to customer demand.

Since steam is used as gasifying agent and due to the high temperature of 1100°C in the gasifier, an almost tar-free product gas with low content of low hydrocarbons of a quality close to synthesis gas has been achieved in a 500 kW pilot plant. The development of the WoodRoll® technology is carried out in three steps, including laboratory scale testing at a 150 kW gasifier unit also involving separate testing of important process parts, pilot scale testing in a 500 kW gasifier, a step to prove the concept, and finally commercialization of the technology with a 5 MW plant at Nordkalk in Köping, Sweden. So far, the technology has been tested in the 150 kW scale and also partly in the 500 kW scale, in Spring 2012, where the gasifier has been operated separately gasifying charcoal with heaters using acetylene as the fuel. The 500 kW gasifier is shown in Figure 6.15. The gas compositions obtained from the tests in the 500 kW gasifier is shown in Table 6.4. No tar or low hydrocarbon was measured in the product gas.

The next step in the development plan will be to integrate all the steps of drying, pyrolysis and gasification, and test the whole process on the 500 kW scale. After proof of concept, the building of the 5 MW plant in Köping will be decided. At Nordkalk in Köping, the produced gas will replace fossil fuels in a limestone kiln.

6.5.1.2.1 Güssing plant

The CHP plant in Güssing, Austria, based on an indirect circulating fluidized bed gasifier, was erected during 2000 to 2001. The plant uses wood chips as the fuel and has a fuel power of 8 MW_{fuel}, converted to 4.5 MW_t heat power and 2.0 MW_e. A process flow sheet of the plant is shown in Figure 6.16.

The biomass is fed into the fluidized bed reactor *via* a rotary valve and a screw feeder system. The reactor is a dual fluidized bed reactor, consisting of two zones a gasification zone and a combustion zone. Steam is used as the gasifying agent and fluidizing medium in the gasification zone. The combustion zone is fluidized with air and provides the heat for the gasification process *via* circulating the bed material. After gasification the produced producer gas is cooled and cleaned in two steps, where the first step includes cooling from 850–900°C to about 160–180°C followed by filtration in a fabric filter to remove particles and some tar. The particles are returned back to the combustion zone of the gasifier. The second step in the cleaning is a scrubber using RME to remove the tar and also reduce the temperature to about 40°C. The used scrubber liquid saturated



Figure 6.15. A photograph of the 500 kW gasifier.

Table 6.4. Gas composition from a test using charcoal in the 500 kW gasifier at 1120°C.

Specification	Vol.-%
H ₂	55–58
CO ₂	12–16
CO	25–31
CH ₄	0–0.5

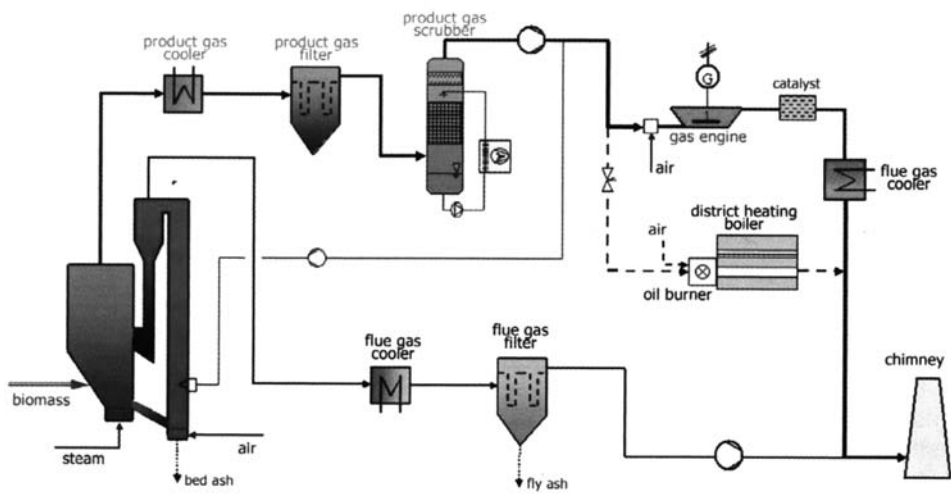


Figure 6.16. Process flow scheme of the Güssing plant (Knoef, 2005).

Table 6.5. Ranges of gas compositions in the dry producer gas (Knoef, 2005).

Product gas composition	Range [Vol.%]
H ₂	35–45
CO	20–30
CO ₂	15–25
CH ₄	8–12
N ₂	3–5

with tar and condensate is vaporized and introduced into the combustion zone to generate heat for the process. The clean fuel gas is thereafter introduced into the gas engine or if the gas engine is not used burned in the boiler. The heat of the flue gas from the engine together with the heat from the combustion zone is used to generate heat for the district heating system.

The gasification process produces a dry producer gas with a constant calorific at about 12 MJ/Nm³. The operation of the plant is experienced as smooth and stable. Table 6.5 shows typical ranges of the producer gas composition.

The Güssing plant is extensively used by many research groups for research and development purposes investigating, for example, in developing new processes for gas cleaning, catalytic upgrading of the fuel gas to chemicals as well as polygeneration systems for heat and power production combined with e.g. production of hydrogen and methane.

Today there are other plants in operation, based on the Güssing technology, e.g. Oberwart, Austria, or under erection, e.g. GoBiGas, Sweden.

6.5.2 Black liquor gasification

The Kraft pulping process accounts for almost 60% of all pulp production i.e. both mechanical and chemical pulp produced globally (Holmberg, 2007). An essential part of the Kraft process is to recover the cooking chemicals and energy from black liquor in the recovery boilers, known as the recovery cycle. This traditional process has proven to work well, but the recovery boiler has several major disadvantages in terms of low electricity generation efficiency, smelt-water explosions and reduced sulfur gas emissions (Whitty, 2005; Larson, 2006). These disadvantages forming the basis for the development of new technologies including black liquor gasification (BLG).

The technologies used for BLG is today mainly fluidized bed gasification (ABB/Alstom and Thermochem processes) or entrained bed gasification where the gas is passing a quencher (Chemrec process). The two different approaches are exemplified in the two subsequent sections below.

6.5.2.1 BL gasification using fluidized bed technology

BLG using fluidized bed technology is either of direct or of indirect gasification types. The indirect gasification was commercialized by MTCI and later Thermochem and consisted principally of two steps. In the actual gasifier, steam is a gasifying medium and heat is provided to the process through steam tubes in the fluidized bubbling bed. The heat in the tubes was supplied by combustion of part of the product gas using pulsed combustion to acquire a good heat transfer. In reality, there were significant problems to reach high enough temperatures in the gasifier. Normally, the temperature was significantly below 650°C, often even below 600°C, which made it difficult to reach sufficient conversion capacity and yield. The steam was used as gasifying media to avoid dilution with nitrogen and to produce a gas with a high heating value.

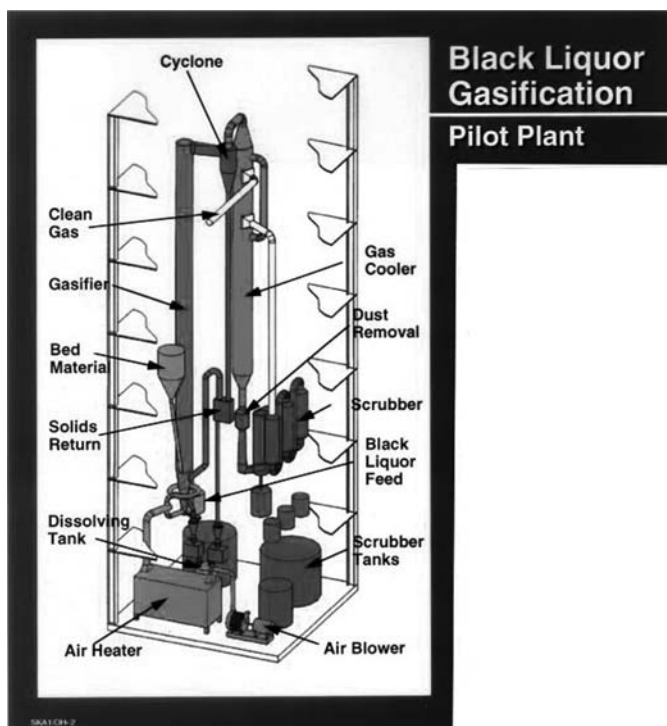


Figure 6.17. Black liquor gasification pilot plant at ABB in Västerås, Sweden.

Later in 1990, ABB Corporate Research in Västerås, Sweden, developed a CFB gasifier with direct partial combustion in the fluidized bed (Dahlquist, 1994). Air was mainly used as gasifying media but principally also enriched air or pure oxygen could also be used. In the nominal 500 kW pilot plant tests were made at different gasification temperatures, relative oxidation (ratio air in relation to what is needed for 100% conversion), dry solids concentration, capacities, type of black liquor and with and without direct caustication using TiO_2 . The process has been patented according to Tanca *et al.* (1992a, 1992b, 1992c).

Initially, the black liquor was introduced into the fluidized bed with bed particles made of Na_2CO_3 . The temperature in the bed was 720°C . Approximately 35% of the air needed to combust the organics of the black liquor was introduced to the gasifier. The sulfates in the black liquor solids were reduced to sulfides, and due to equilibrium constraints also a major part of the sulfides were evaporated as H_2S . The H_2S was absorbed in a gas scrubber using Na_2CO_3 and NaOH . To avoid simultaneous absorption of carbon dioxide, a selective absorption process, approximately 20 times more effective towards H_2S was developed. The remaining H_2S is converted into SO_3 during the combustion in the gas turbine, so no hazardous gas is emitted. Later on addition of TiO_2 was tested to achieve so-called direct caustication. In this case CO_2 is stripped off from the Na_2CO_3 forming Na_2O combined with TiO_2 , forming $\text{Na}_2\text{O} \cdot \text{TiO}_2$. This removed the need for a separate lime kiln for reburning of CaCO_3 as is normally needed in the Kraft process.

The CFB, shown in Figure 6.17, was equipped with two cyclones in series for removal of solids. The solids were reintroduced to the bed through G-valves from the down comer. After the cyclones, the gas was cooled by a couple of heat exchangers with water-cooling. A bag house removed most of the remaining particles and thereafter the gas was scrubbed in a two-step counter-current scrubber. The gas was finally combusted in a natural gas burner. Prior to entering the gasifier the air was heated to approximately 400°C , and the black liquor was heated to approximately 120°C , to make it easy to pump.

Table 6.6. Results from simulations with polynoms made from real plant operations and physical relations. These are compared with equilibrium calculations.

Input data															
No	[%DS]	tDS/ [m ² h]	[Relox]	<i>T</i> _{bot} [°C]	<i>T</i> _{inj} [°C]	CO [%]	H ₂ [%]	CO ₂ [%]	H ₂ O [%]	CH ₄ [%]	H ₂ S [%]	SO ₄ red [%]	H ₂ S _{strip} [%]	<i>C</i> _{conv} [%]	HHV _{drygas} [KJ/Nm ³]
Dry gas composition															
1	70	1.8	35	700	695	2.7	11.5	13.1	26.7	1.3	0.63	91.3	50.7	92.8	2066
2	70	1.8	45	700	695	2.3	9.2	11.9	25.5	1	0.59	91.9	53.9	94.3	1668
3	70	2.4	35	700	695	2	9.9	11.7	27	1.4	0.78	86.9	58.5	78	1848
4	70	1.2	35	700	695	2.9	11.5	14	26.4	1.1	0.61	93.3	50	98.9	2036
5	70	1.8	35	670	650	3.1	11.6	12.1	24.2	1.3	0.8	88.5	60.2	84.5	2118
6	70	1.8	35	725	720	3.2	14.5	12.1	27.4	1.5	0.48	92.2	41.9	97.6	2537
Dried gas composition															
7	70	1.8	35	700	695	3.2	13.6	15.6	13	1.5	0.75	91.3	50.7	92.8	2458
8	70	2.4	35	725	720	2.4	13.5	13.7	15.8	1.9	0.73	87.9	49.7	82.5	2456
9	70	1.8	35	725	720	3.8	17.3	14.4	13.5	1.8	0.57	92.2	41.9	97.6	3022
ref equilibrium calculations															
	70		36		725	6.5	13.3	10.8	13	0	1.06				2800
	70		45		725	4.2	9	11.1	13.2	0	0.95				2100
	70		36		675	7	13.5	16.4	17.5	0	1.33				2800

No = number, %DS = % dry solids, Relox = % oxygen added of amount needed for 100% oxidation, T_{bot} = Tempe at bottom, T_{inj} = Temp at injection point. C_{conv} = % of all carbon that has been converted into gaseous compounds, DS/m² h = tonne dry solids/m² h in the reactor.

Table 6.6 presents some results from the pilot plant tests compared with equilibrium calculations for different operational conditions. The equilibrium calculations predict no CH₄ in the produced gas, while the true experiments give significant amounts. In reality the equilibrium calculations still give the same trends as for real operations but with a translation from temperatures around 200°C below the pilot plant operations. The total heating value of the gas still is similar, but with another gas composition. Due to the high salt content, a significant catalytic effect is obtained and therefore almost no tars are detected in the gas.

Due to financial problems at the end of the 1990s ABB decided not to scale up the technology further to a full-scale operational plant. Instead, ABB sold their activities in the power plant business to Alstom Power. Today there are attempts to develop the technology at Bioregional Minimills in Manchester, UK, in cooperation with Mälardalens University and KTH.

6.5.2.2 BL gasification using entrained flow technology

Black liquor gasification using entrained flow technology has been used for many years as an alternative to recovery boilers but has yet not really "taken off". SCA-Billerud was running a full-scale gasification plant at SCA Ortviken between 1970 and 1986. In this case, an entrained bed was used with a residence time of only a few seconds in the reactor. The heat from the black liquor then was not enough so they had to use additions of oil to get the process running. The reactor had injection of black liquor together with oil in the upper center and air was introduced around it. Still, as the residence time was short, much of the produced char was not converted, which made the process poor with respect to the energy balance. Still, the process was operated for 16 years. The operating temperature was around 725°C and thus most of the material was solid particles. All the material problems were handled in the reactor and proved that at least 725°C was practical for long-term operations using Högånäs bricks as insulation inside the reactor. The gas from the reactor was cooled in a Waste Heat Boiler (WHB) to approximately 150°C. The gas then was passing a Venturi scrubber to remove solid particles. The gas then was

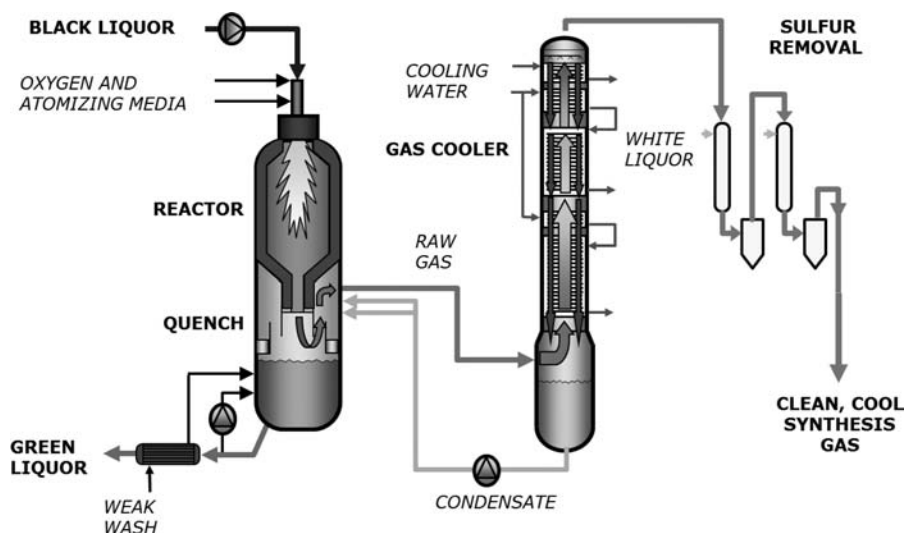


Figure 6.18. The Chemrec process layout.

combusted to oxidize the H_2S into SO_2 , which was absorbed in another scrubber and used in the Ca-sulfite process.

The major problem with the process was that the conversion of carbon was in the range 65% and thus organics should be reused. Solids was thus filtered and pressed before it was reintroduced to the reactor. As the dry solids content was only around 12%, the energy to evaporate the water was very negative and thus more oil was added. The energy economy thus became less favorable especially when the oil price increased. Four other plants were built in France, Spain and the US. The main conclusion from experiences was that the energy cost was high and thus the economy not that good. To achieve a better efficiency it was concluded that either the temperature should be increased or the residence time.

The Chemrec process is a development of the entrained technology where the gasification takes place at around 1000°C in a quencher reactor, and all solid material is melted. The droplets are dissolved in the liquor in the quencher, while the gas is released and passed through a scrubber to remove salts. The operating pressure is 27–30 bar, which is suitable especially if the gas should be used for synthesis of methanol or DME, which is the purpose with this process today. A pilot plant has been in operation at Smurfit Kappa pulp and paper mill in Piteå in northern Sweden. The pilot has been in operation day and night since 2006, and the technology is now proven with respect to the actual gasification. A process layout of the process is shown in Figure 6.18. The plant in Piteå had 11,500 hours operation in December 2009. In July 2010, a DME plant was installed to convert the syngas into DME for vehicle use. Since 2010, also a DME plant is placed in connection to the gasifier. This is now being verified for long-term operation. The plan was to build a full-scale demo plant in Örnsköldsvik but due to a decision by the new owners of Domsjö sulphite plant, this project was cancelled in 2012.

Today Chemrec is offering a number of commercial products. They have 150–300 tonnes/day atmospheric air-blown boosters that should be installed in parallel to existing recovery boiler to overcome bottle necks. The next product is an atmospheric oxygen-blown booster up to 450 tonnes/day giving an energy richer gas, suitable for replacement of oil in lime kilns. For slightly larger plants, 500–550 tonnes/day, a pressurized oxygen-blown unit is offered. Finally large scale pressurized oxygen-blown plants, about 1000–4000 tonnes/day, are offered to replace existing recovery boilers or for green field mills. This type of plant can be as combined cycle units or including production of DME or methanol from the gas.

6.6 MODELLING OF GASIFICATION SYSTEMS

The efficient operation of a biomass gasifier depends on a number of complex chemical reactions, including fast pyrolysis, partial oxidation of pyrolysis products, gasification of the resulting char, conversion of tar and lower hydrocarbons, and the water gas shift reaction. To establish design data is a therefore a complex task including experiments as well as modeling or process simulations. Experimental data are more reliable than data obtained from modeling or simulations but are generally very expensive to acquire, especially at large scale. Another major drawback of data obtained from experiments is their limited use, i.e. the data are in general only valid for the specific experimental conditions chosen. If any of the original process or parameters changes, such as the size of the gasifier, the optimum operating conditions are no longer valid.

Simulation, or modeling, of a gasifier may not give a very accurate prediction of its performance, but can at least provide with a qualitative guidance on the effect of design and operating or feedstock parameters. Therefore, a good combination of experiments and modeling is essential for a reliable design of a gasifier. Simulation or mathematical modeling may provide with information about (Basu, 2010):

- The optimum operating conditions or a design for a gasifier;
- Identify the areas of concern or danger in the operation;
- Provide with information on extreme operating conditions (high temperature, high pressure) where experiments are difficult to perform;
- Provide with information over a much wider range of conditions than one can obtain experimentally;
- Improve the interpretation of experimental results and analyses abnormal behavior of a gasifier;
- Assist in the scale-up of the gasifier from one successfully operating size to another, and from one feedstock to another.

Gasifier simulation or mathematical models may be classified into the following groups:

- Material and energy balance models
- Kinetic
- Thermodynamic equilibrium
- Computational fluid dynamics (CFD)
- Artificial neural network.

In the subsequent sections, the first three modeling approaches will be briefly described together with a few examples of modeling examples.

6.6.1 Material and energy balance models

Material and energy balance models are the simplest models, conceptually, but provide with input data to other models as well as predict the overall performance of a particular gasifier. Input data to a material and energy balance model is easily obtained from a fuel analysis. However, some consideration is needed in the development of the model. For instance, not all fuel fed into the gasifier is converted to product gas, since part is lost in the form of non-reacted char as well as in the combustion process to produce heat for the process.

An overall material balance for a gasifier could be outlined as exemplified by Gómez-Barea and Leckner (2010):

$$F_{f,in} = F_f(1 + \xi_u + \xi_b) \quad (6.12)$$

where:

$F_{f,in}$ = the fuel input into the reactor [kg/s]

F_f = the gas produced [kg/s]

ξ_u = factor to account for loss due to unreacted char [kg/kg fuel converted]

ξ_b = factor to account for fuel burned to provide with heat for the process and to compensate for heat losses [kg/kg fuel converted].

Expression (6.12) can then be divided into the components ashes, a , moisture, w , and combustibles, b , where ($a + w + b = 1$) if the quantities are in kg/kg fuel, as follows:

$$F_{f,in} = F_f a(1 + \xi_u + \xi_b) + F_f w(1 + \xi_u + \xi_b) + F_f b(1 + \xi_u + \xi_b) \quad (6.13)$$

If only H_2O is considered for the gasification of the char, the quantity of gas, F_g , will consist of the not burned volatiles and the gas produced by gasification of char by H_2O both representing the amount of fuel converted $F_f b$. Contributing to F_g is also the fuel moisture w and the flue gas from the combustion. The quantity F_g can be expressed as:

$$F_g = F_f b + F_{f,in} w + F_f b \xi_b g_0 \quad (6.14)$$

where g_0 is the flue gas produced by combustion of a kg of the part of the fuel that burns, $F_f b \xi_b$. A heat balance over the reactor can provide with the amount of fuel, ξ_b , needed to produce the heat for the process and reach the temperature T_b :

$$F_f b \xi_b H_{u,b} = F_{f,in} h_f(T_b) + F_{f,in} w H_w + F_f b \xi_b l_0 h_{air}(T_b) + F_f b x_c \varphi_g h_{H_2O}(T_b) MM_{H_2O}/MM_c \\ + (\text{loss to surroundings}) \quad (6.15)$$

The terms on the right side are the heat quantities required for: two terms for heating of fuel to bed temperature, air for combustion and steam for gasification and losses to the reactor. $H_{u,b}$ represents the heating value of the fuel burned, which could be either the volatiles or the char. The other variables are:

φ_g = amount of gas produced by gasification; this is not known.

x_c = the char fraction. x_c is determined by a standard analysis of the fuels content of volatiles

The heating value of the volatiles, $H_{u,v}$, can be expressed by:

$$H_{u,v} = (H_{u,f}/b + x_c H_{u,c})/x_v \quad (6.16)$$

where $H_{u,c}$ and $H_{u,f}$, represent the heating value for the char and the fuel, respectively. $H_{u,f}$ is given by the fuel analysis. x_v is the fraction of the fuels volatiles and $x_c + x_v = 1$. The heating value of the producer gas is defined as the energy contained in the volatiles $F_f b(1 - x_c \varphi_g)$ and in the gas from the gasification of char, $F_f b x_c \varphi_g$, i.e.:

$$F_g H_{u,g} = F_f b(H_{u,v}(1 - x_c \varphi_g) + H_{c,g} x_c \varphi_g) \quad (6.17)$$

Other useful quantities such as the air ratio, λ , may also be calculated using the following expression:

$$\lambda = F_f b \xi_b l_0 / F_{f,in} b l_0 = \xi_b / (1 + \xi_u + \xi_b) \quad (6.18)$$

The derived expressions can be used to analyze and predict different quantities for a gasification process. Further assumptions need to be done depending on if a so-called indirect (allothermal) or direct (autothermal) gasifier is considered. In a direct gasifier, as for example BFB or CFB shown in Figure 6.19, the volatiles is assumed to burn in the first place and that char is consumed only after depletion of the volatiles. In such case is $H_{u,b} = H_{u,v}$ and all char not gasified is lost, $\xi_u = x_c(1 - \varphi_g)$. If an indirect gasifier is considered, such as the twin bed shown in Figure 6.19, bed material is transported between the combustor reactor and the gasifier. In the combustor is only the char burned and the heat is transferred to the gasifier with the hot bed material. In this case is $H_{u,b} = H_{u,c}$ and therefore the third term on the right disappears in expression (6.15). The char loss is in this case $\xi_u = x_c(1 - \varphi_g) - \xi_b$.

Material balance models can also be used for modeling the gas composition if included in a model based on statistical experimental data and also certain assumption about simulating the hydrocarbon is made. In this case, the model is sometimes referred to as empirical models. This approach is exemplified below.

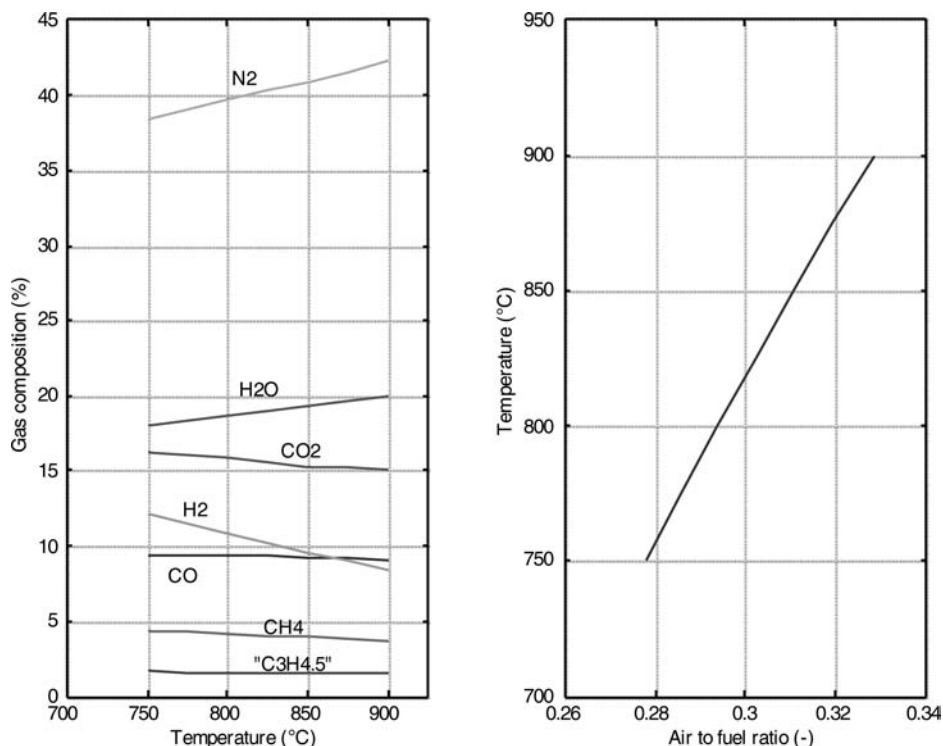


Figure 6.19. The composition of the product gas as function of the air-to-fuel ratio.

6.6.1.1 An empirical model for bubbling fluidized bed gasification

When modeling fluidized bed gasification of biomass, one of the most difficult tasks is to predict the concentrations of methane and the higher hydrocarbons in the product gas. This aspect is of importance, as these compounds tend to be the most important species with respect to energy content. Additionally, as these compounds are energy rich, inaccuracies in the predictions of these may cause large errors in subsequent temperature predictions; errors that in turn strongly will influence reaction rate computations. The methane content in the product gas during fluidized bed gasification of biomass tends to be (much) higher than what the equilibrium suggests. This implies that for being able to model and predict the concentrations of methane (and the higher hydrocarbons) empirical or semi-empirical expressions must be employed.

At KTH a large number of bubbling fluidized bed tests have been carried through over the years. Analysis of these tests gave that methane concentrations, expressed as being the mole fraction of methane relative to total methane, carbon monoxide and carbon dioxide, tended to vary between 0.10 and 0.17. It was further possible, with some uncertainty, to derive an expression that gives the methane concentration as a function of the carbon monoxide, carbon dioxide and hydrogen concentrations. In turn was it also possible to link the concentration of the higher hydrocarbons to that of methane.

The product gas is assumed to consist of carbon monoxide, carbon dioxide, water, hydrogen, nitrogen, methane and higher gaseous hydrocarbons, given as the pseudo hydrocarbon "C₃H_{4.5}". Thus, eight unknowns including the temperature will be computed. This, for a given air/fuel-ratio, by solving the (independent) balances for carbon, hydrogen, oxygen and nitrogen and heat respectively and by assuming that the homogenous water gas shift reaction (Eq. 6.6) will be at equilibrium. For solving the system two more empirical statistical equations for the methane

and the tar is needed. These equations (6.19) and (6.20) are derived from a large number of experimental data from several test runs.

$$C(\text{CH}_4) = 0.19 \cdot C(\text{CO}) + 0.087 \cdot C(\text{CO}_2) + 0.090 \cdot C(\text{H}_2) \quad (\text{Methane}) \quad (6.19)$$

$$C(\text{C}_3\text{H}_{4.5}) = 0.65 + 0.27 \cdot C(\text{CH}_4) \quad (\text{Tar}) \quad (6.20)$$

C is here the concentration in percentage.

Figure 6.19 shows the modeling result when biomass is gasified with air. In the example, the temperature of the in-going air is 25°C, illustrating the varying of the composition of the product gas as function of the air-to-fuel ratio.

6.6.2 Kinetic models

Kinetic rate models generally provide with accurate and detailed information on kinetic mechanisms describing the conversion during biomass gasification. This information is important for the design, evaluation and improvement of a gasifier. One drawback is that the modeling is computationally very intensive (Sharma, 2008).

In general, a kinetic model investigates the development of reactions in a gasifier, providing the product composition at different positions along the reactor. Both geometrical factors as well as hydrodynamics of the gasifier are considered. Since kinetic rate expressions, including reaction rate, residence time of particles and hydrodynamics, are obtained from experiments, the simulation of experimental data is superior compared to equilibrium modeling. This is in general true for reactions taking place at low operating temperatures, <800°C, since the reaction rate is slower at these temperatures and therefore a longer residence time for complete conversion is needed (Altafini, 2003). Also, since kinetic rate models always contain parameters that are gasifier-specific, it will limit their applicability to different plants.

Modeling of the reaction kinetics requires a simultaneous computation of the bed hydrodynamics as well as mass and energy balances to obtain yield of gas, tar and char at a given operating condition. During the progress of the gasification, the biomass particles are affected by the environment and are first transformed to char and then further reduce its size due to the gasification process. This transformation may be manifested as a size reduction with unaffected density or reduction in density with unaffected size. To address this three main different modeling approaches have been developed: shrinking core model, shrinking particle model and volumetric model.

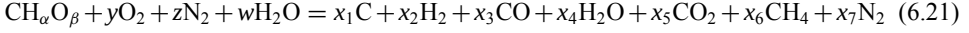
The hydrodynamics of the reactor is required since reaction kinetics reflects the physical mixing process and could be defined as follows (Basu, 2010):

- Zero dimensional (stirred tank reactor)
- One dimensional (plug flow)
- Two dimensional
- Three dimensional.

Kinetic models are sensitive to the gas and solid interactions in the gasifier and therefore the models could be divided into the different types of reactor technology, i.e. fixed bed fluidized bed or entrained flow.

To illustrate kinetic modeling, an example of a kinetic model, adapted from Wang and Kinoshita (Wang, 1993), is briefly outlined below. The model is based on kinetics of surface reactions and focus on simulating the overall gasification process by kinetics of surface reactions in the char reduction zone of a downdraft gasifier. The following parameters were evaluated: type of oxidant, residence time, char particle size, temperature, pressure and equivalent ratio (*ER*) and moisture. For simplicity, the model states that the biomass first enters the pyrolysis zone, where the biomass is converted to volatiles and char and then moves to the char reduction zone (CR). The combustion zone is neglected since the gasification is much slower and thus the

overall gasification is controlled by the kinetics in the CR zone. Biomass gasification could be expressed as:



When the products from the pyrolysis zone enter the CR zone (time $t = 0$) the following applies referring to expression (6.21):

$$x_{2,0} = 0; \quad x_{3,0} = 0; \quad x_{7,0} = z$$

$$x_{1,0} + x_{5,0} + x_{6,0} = 1 \quad (6.22)$$

$$2x_{4,0} + 4x_{6,0} = \alpha + 2w \quad (6.23)$$

$$x_{4,0} + 2x_{5,0} = 2y + \beta + w \quad (6.24)$$

where $x_{i,0}$ is the initial amount of component i in the CR zone, y is a function of ER and w can be calculated from the moisture in the biomass. To be able to solve the equations (6.22)–(6.24) an additional expression is needed as follows:

$$x_{4,0} = \lambda x_{5,0} + w \quad (6.25)$$

λ is here the formation ratio for vapor/ CO_2 and is assumed to be 1, which means that the same amount of CO_2 and H_2O is formed in the pyrolysis zone. The water is added to the amount already present in the biomass.

For the chemical reactions in the CR zone, it is assumed that the gasification takes place at a temperature below 900°C and therefore the mass transfer and the pore diffusion can be considered as faster than the chemical reactions. In addition, the water gas shift reaction, reaction (6.6) above, is omitted since experiments indicated that the model was not sensitive to the apparent rate constant for this reaction. The reactions considered in the model were: (i) the Boudouard reaction, reaction (6.3), (ii) the water gas reaction, reaction (6.4), (iii) $\text{C} + 2\text{H}_2 \leftrightarrow \text{CH}_4$ and (iv) the steam reforming, reaction (6.5).

For the surface reactions a Langmuir-Hinshelwood mechanism (reference) was applied for reaction (6.1) and (6.2) and the Langmuir-Riedel mechanism was applied for reaction (6.3) and (6.4). The rate equations were formulated based on these mechanisms assuming a spherical form of the char particles, and that the number of active sites of the surface is proportional to the surface area. The final rate equations for the 4 reactions become:

$$-v_1(X) = k_{a1} \frac{x_5 - x_3^2/(P_X K_{p1})}{\sum (K_i + 1/p)x_i} \left(\frac{x_{1,0}}{x_1} \right)^{1/3} \frac{x_1}{\rho d_p} \quad (6.26)$$

$$-v_2(X) = k_{a2} \frac{x_4 - x_3 x_2/(P_X K_{p2})}{\sum (K_i + 1/p)x_i} \left(\frac{x_{1,0}}{x_1} \right)^{1/3} \frac{x_1}{\rho d_p} \quad (6.27)$$

$$-v_3(X) = k_{a3} \frac{x_2^2 - x_6 P_X / K_{p3}}{P_X \sum (K_i + 1/p)x_i} \left(\frac{x_{1,0}}{x_1} \right)^{1/3} \frac{x_1}{\rho d_p} \quad (6.28)$$

$$-v_4(X) = k_{a4} \frac{x_4 x_6 - x_3 x_2^3/(P_X^2 K_{p4})}{P_X \sum (K_i + 1/p)x_i} \left(\frac{x_{1,0}}{x_1} \right)^{1/3} \frac{x_1}{\rho d_p} \quad (6.29)$$

The $v_i(X)$ is the net reaction rate, K_{pi} is the equilibrium constant, P_X and p is the pressure in the CR zone, and k_{ai} is the apparent rate constant for reaction i . The apparent rate constant, k_{ai} , is the product of the pre-exponential factor and the exponential factor according to the Arrhenius equation.

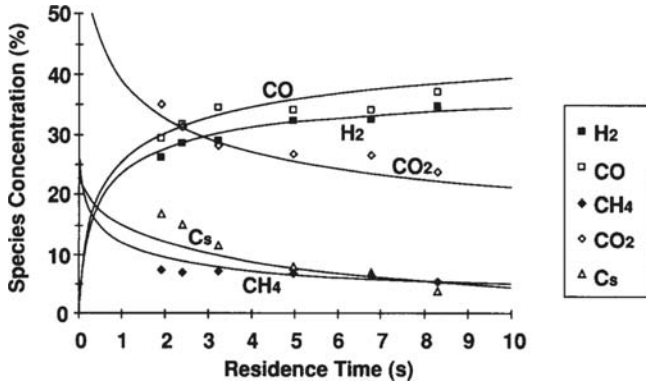


Figure 6.20. Residence time vs. species concentration (Wang, 1993).

Finally, a set of differential equations apply to the gasification reactions in the CR zone:

$$\frac{dx_1}{dt} = v_1(X) + v_2(X) + v_3(X) \quad (6.30)$$

$$\frac{dx_2}{dt} = -v_2(X) + 2v_3(X) + 3v_4(X) \quad (6.31)$$

$$\frac{dx_3}{dt} = -2v_1(X) + v_2(X) + v_4(X) \quad (6.32)$$

$$\frac{dx_4}{dt} = v_2(X) + v_4(X) \quad (6.33)$$

$$\frac{dx_5}{dt} = v_1(X) \quad (6.34)$$

$$\frac{dx_6}{dt} = -v_3(X) + v_4(X) \quad (6.35)$$

From the equations, it can be deduced that the product gas depends on the temperature and the pressure of the gasifier the moisture/biomass ratio, ER , the amount of nitrogen, the particle size and the residence time. A typical result for the species concentration dependency of the residence time is shown in Figure 6.20.

6.6.3 Equilibrium models

Thermodynamic models are independent of the gasifier and are therefore more flexible and suitable for process studies of the most important process parameters. Unlike the kinetic models, no information about the influence of the hydrodynamic and geometric parameters can be obtained. Thermodynamic equilibrium modeling is today mainly based on methods where Gibbs free energy is minimized. At the minimum of Gibbs free energy, the reacting system is at its most stable composition and thus in chemical equilibrium. However, there should always be an awareness that thermodynamic equilibrium may not be reached for all processes within the gasifier mainly due to the relatively low operation temperatures in many gasification processes with product gas outlet temperatures ranging from 750 to 1000°C (Bridgwater, 1995). As pointed out by Villanueva *et al.* (2008), thermodynamic equilibrium modeling is a good approach in case of entrained flow gasifiers and also in some cases for downdraft fixed bed gasifiers when a high enough temperature is achieved throughout (Puig-Arnavat, 2010). Generally, the temperature needs to be above 1200°C

for the model approach to be valid (Altafini, 2003). When analyzing gasification processes at lower temperatures, using equilibrium modeling, the analysis of results should be carried out with some precaution. To compensate for non-equilibrium effects or reactions several approaches with so-called semi-empirical methods to solve the problem has been used. In these models are a non-equilibrium effects tackled by adding e.g. correlations based on empirical data. A very common equilibrium problem is the prediction of methane, which is not at equilibrium. Correction for this the application of empirical parameters in order to modify the carbon conversion or it is possible to correct directly the methane fraction in the syngas (Li, 2001).

Equilibrium modeling can generally be divided into a stoichiometric and a non-stoichiometric equilibrium models (Basu, 2010). The stoichiometric approaches require a clearly defined reaction mechanism incorporating all reactions and species involved. A typical model includes a mass balance for the overall reaction of all species and the expressions for the equilibrium constants for the particular reactions occurring during the gasification process. These two sets of equations are then solved and provide with the yield and the product of the process for a given air/steam-to-biomass ratio.

In case of a non-stoichiometric model, no particular reaction mechanisms or species are involved in the simulation. The only input needed to specify the feed is the elemental composition of the biomass, which can be readily obtained from ultimate analysis data (Li, 2004). Below is non-stoichiometric modeling illustrated as outlined by Jarungthammachote and Dutta (2008), where the gas composition of gasification is determined at certain operating conditions. The gasification is assumed to be carried out with small biomass particles to easily reach equilibrium.

The total Gibbs free energy of a system is defined as:

$$G^t = \sum_{i=1}^N n_i \mu_i \quad (6.36)$$

where G^t is the total Gibbs free energy and n_i is the number of moles of species i . The Gibbs free energy, originally called available energy, was developed in the 1870s by the American mathematician Josiah Willard Gibbs. In 1873, Gibbs described this “available energy” as the greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition. μ_i is the chemical potential of species i and is given by:

$$\mu_i = \overline{G}_i^o + RT \ln\left(\frac{\phi P_i}{P^o}\right) \quad (6.37)$$

where f_i represents the fugacity of species i . The superscript o denotes a standard thermodynamic quantity, and $\overline{G}_i^o$ and P^o are the standard Gibbs free energy and the standard pressure of species i , respectively. ϕ is the fugacity coefficient. If all gases are assumed as ideal gases at a pressure of one atmosphere, expression (6.37) can be rewritten as:

$$\mu_i = \overline{G}_{f,i}^o + RT \ln(y_i) \quad (6.38)$$

where $y_i = n_i/n_{tot}$ which is the mole fraction of gas species i . $\overline{G}_{f,i}^o$ is the standard Gibbs free energy of formation of species i and is set equal to zero for all chemical elements. If (6.38) is substituted into (6.36) the resulting expression is:

$$G^t = \sum_{i=1}^N n_i \overline{G}_{f,i}^o + \sum_{i=1}^N n_i RT \ln\left(\frac{n_i}{n_{tot}}\right) \quad (6.39)$$

The problem is to obtain the values of n_i which minimize the objective function G^t . The proper method, which is usually performed for the minimization of the Gibbs free energy problem, is

the Lagrange multipliers. The limitation of this problem is the elemental balance:

$$\sum_{i=1}^N a_{ij} n_i = A_j \quad \text{for } j = 1, 2, 3, \dots, k \quad (6.40)$$

where a_{ij} is the number of atoms of the j th element in a mole of the i th species. The value of n_i should be obtained such that G^t is at minimum. By using the Lagrange multiplier method the Lagrange function L is defined as:

$$L = G^t - \sum_{i=1}^N \lambda_j \left(\sum_{i=1}^N a_{ij} n_i - A_j \right) \quad (6.41)$$

where λ_j is the Lagrangian multiplier for the j th species. The extreme is obtained by dividing (6.41) with RT , substituting G^t with (39) and take the derivative, $\partial L / \partial n_i = 0$:

$$\frac{\partial L}{\partial n_i} = \frac{G_{f,i}^o}{RT} + \sum_{i=1}^N \ln \left(\frac{n_i}{n_{tot}} \right) + \frac{1}{RT} \sum_{i=1}^N \lambda_j \left(\sum_{i=1}^N a_{ij} n_i \right) = 0 \quad (6.42)$$

In the example below, the software tool ASPEN plus is used where all possible reactions in a reactor the balance between all the reactions is calculated using the Gibbs free energy method.

6.6.3.1 Simulations using an equilibrium model compared to experimental data

Modeling using equilibrium calculations can be illustrated by a study carried out by Dahlquist *et al.* (2012). In this study the impact of different process parameters on the gas composition in biomass gasification in CFB was investigated.

Operational aspects were modeled using equilibrium calculations in combination with stoichiometric physical models, including energy and mass balances, and statistical models, like partial least square (PLS) models. Real process aspects like kinetics and the difference in product gas quality as a function of temperature, load and relative oxidation during the gasification was included. The direct system design was addressed using equilibrium calculations with ASPEN plus using the two simple reactor models; one RYIELD reactor as the decomposer and one RGIBBS. The main strategy of solving the case is the Gibbs free energy minimization of the components. Experimental data from pilot plants and real gasification processes using different fuels and operation conditions was used in both the statistical models and for parameter adjustments in the ASPEN plus modeling.

The equations used in the physical simulation model of the gasifier were primarily stoichiometric and are illustrated by equations (6.43–6.45)

$$\frac{\partial m_{inventory}}{\partial t} = \sum m_{i,in} - \sum m_{i,out} \quad (6.43)$$

$$\frac{\partial c_i}{\partial t} = \sum (c_i \cdot m_j)_{in} - \sum \frac{(c_i \cdot m_k)_{out}}{m_{inventory}} \quad (6.44)$$

$$\frac{\partial T_{inventory}}{\partial t} = \frac{(\sum T_j c_{p,i} c_i m_{jin}) - (\sum T_j k c_{p,i} c_i m_{jout}) + (H - UA(T_{inventory} - T_{outside}))}{m_{inventory} (\sum c_i c_{p,i})} \quad (6.45)$$

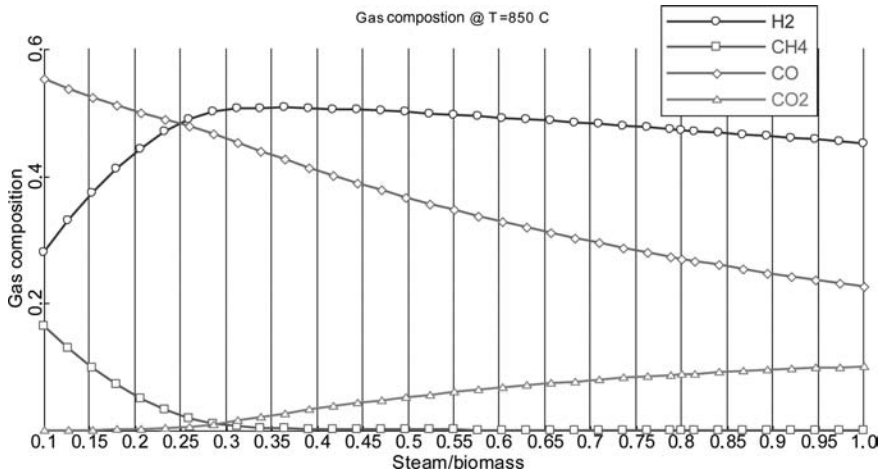


Figure 6.21. Effect of steam to biomass ratio on content of different gas components from equilibrium calculations at 850°C.

The parameters represent:

$m_{i,in}$ = mass input flow of each single component i (C, H, O, N, CO₂, H₂O, NO₂, ash)

$m_{i,out}$ = is the corresponding output flow of $m_{i,in}$

$m_{inventory}$ = total mass flow in the bed inventory

j = all incoming flows of the inventories

k = all outgoing flows of the inventories

$T_{inventory}$ = temperature in the inventory calculated from the energy balance

ΔH = energy released during combustion

U = overall heat transfer coefficient

A = heat exchanger area

$T_{outside}$ = temperature at the other side of the heat exchanger surface

$c_{p,i}$ = heat capacity for each component i .

The model was validated against experimental data from CFB gasification tests (Dahlquist, 2005) using biomass feedstocks as well as black liquor. Table 6.6 in chapter 6.5.2.1 illustrates the data from the combined model and the equilibrium calculations. The results clearly display that the effect of doubling the load is significant in reality, but without any impact for the equilibrium model. Moreover, in case of methane, the equilibrium model indicates no methane production, while experiments and the combined model is showing some 1–1.5% at 650–725°C. This can be expected when using equilibrium calculations since reactions for formation of CH₄ is not in equilibrium at the actual temperatures.

The calculated gas composition when the gasification temperature is fixed at 850 °C and 752°C, respectively, as the steam-to-biomass ratio changes from 0.1 to 1 are shown in Figure 6.21 and 6.22. The result shows that the H₂ value increases up to steam-to-biomass ratios around 0.3 for 850°C and to 0.55 for 752°C and thereafter slowly decreases. In case of CH₄ the concentration starts at a high value at low steam-to-biomass ratio, but is then decreasing as the steam content is increasing. It is evident that if the water content is very high a lower CH₄ production can be expected at a given temperature.

Figure 6.23 exemplifies the effect of pressure at constant temperature and steam-to-biomass ratio. A slight decrease in CO and H₂ as well as an increase in CO₂ and CH₄, as the pressure is increased is observed. The effect of pressure is quite small.

The main conclusion of the simulations was that by reducing the steam-to-biomass ratio and the temperature as well as increasing the pressure and the load it is possible increase the CH₄ content in the product gas.

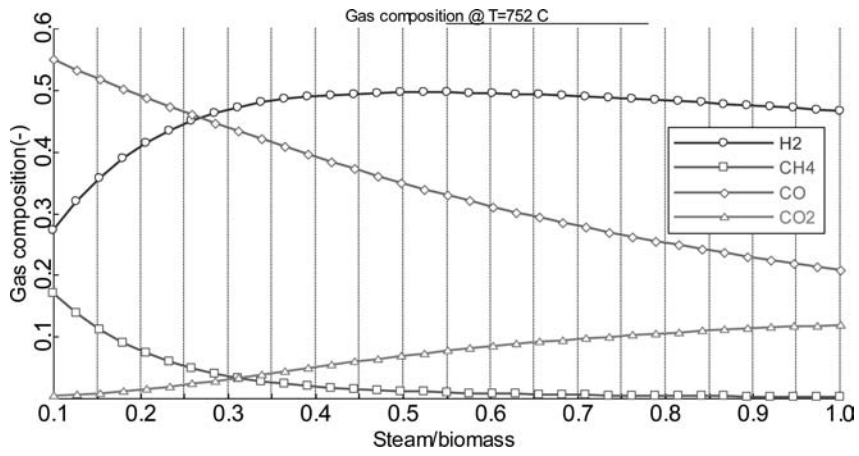


Figure 6.22. Effect of steam to biomass ratio on content of different gas components from equilibrium calculations at 752°C.

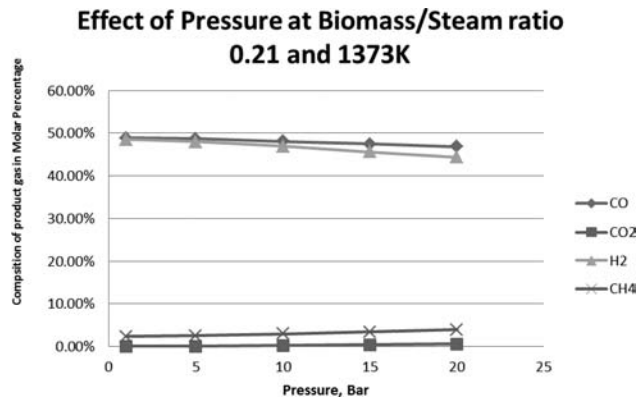


Figure 6.23. Gas composition as a function of pressure at constant steam-to-biomass ratio 0.21 and temperature 1373 K.

6.7 OUTLOOK

Although the commercialization interest of small to large scale cost-effective and competitive gasification plants for utilizing biomass and black liquor has increased over the last 10 years, today's industrial stakeholders hesitate in investing in the technology. One reason is that no single stakeholder wants to take the whole economic and technical risk for the initial implementation of the technology. This is in particular true for the implementation of large scale plants. It is well known that after the first commercial size plant of a new technology has been built, the following plants will cost less due to learning effects, i.e. the gained knowledge and experience will improve the design and operation of new succeeding plants. Therefore it is exceedingly important that the society financially support the establishment of demonstration projects such that no single party has to bear the entire risk and also support in setting-up an appropriate risk handling strategy for the subsequent plants.

Another challenge is to bring the emerging thermal conversion technologies closer to the power generation or chemicals production processes, with both sides of the interface moving to an acceptable middle position. Also, bio-energy systems will in many cases be relatively small, although still more complex than corresponding small scale combustion power plants, and must therefore be technically and economically competitive at much smaller scales of operation than the process and power generation industries are used to handling.

Some general aspects of importance for the implementation of gasification technologies utilizing biomass and black liquor will be briefly described below.

6.7.1 Biomass gasification

Although the basic gasification process principles are well developed a successful commercial implementation of gasification technologies utilizing biomass requires bridging of important knowledge gaps. A number of technical as well as economic issues need to be addressed:

- Since there is a number of technologies for thermochemical conversion, upgrading as well as end-user applications there is a need for extensive and systematic techno-economic analyses to identify the best practice depending on the conditions, such as available feedstock, existing infrastructure and product needed.
- There is a need to increase the competence and awareness of new technologies among end users. The technology end-users need to be convinced about the economic and environmental advantages of implementing new technologies.
- Other more hands-on technical issues are, for example, ash related operational problems, syngas quality, alkali volatilization, tar as well as limiting speciation and concentrations of critical syngas impurities.

It is interesting to note from the literature that identified important knowledge gaps and technical challenges have been the same for some time, implying that the progress so far has been limited. New more or less successful technologies and mitigations have been developed to solve the problems, however, in general associated with higher costs.

6.7.2 Black liquor gasification

There are a number of black liquor pilot scale plants in operation today e.g. Weyerhaeuser's 300 tonnes/day low pressure, entrained flow booster gasifier in New Bern, North Carolina, Georgia-Pacific's 200 tonnes/day fluidized bed steam reformer system in Big Island, Virginia, Norampac 100 tonnes/day steam reformer in Trenton, Ontario, and Chemrec's 20 tonnes/day pressurized, oxygen-blown entrained flow gasification development plant in Piteå, Sweden (Naqvi, 2010). To take the technology the next steps for implementation of biorefinery operations at the integrated BLG pulp mills there are, however, some issues to be addressed before achieving this goal.

On the technical side BLG may produce a green liquor with a lower concentration of NaOH compared to the corresponding liquor from the recovery boiler. This has to be compensated by adding more NaOH to the green liquor to receive the white liquor. Other major potential impacts include pulp yield, steam and electricity balance, as well as synthesis gas treatment processing. These issues can be resolved by determining the best approaches and advanced pulping technologies. To achieve a synthesis gas required for downstream processing selected techniques must be demonstrated for gas cleanup and conditioning to reduce e.g. tar concentrations to acceptable levels.

Selection of appropriate conversion technologies for producing fuels, electricity and chemicals from the synthesis gas is essential. The preferred choice between electricity and fuel as the final end product is partially a strategic decision of the host pulp mill to implement BLG technology replacing conventional recovery cycle and partially an economic optimization. Countries with a significant forestry industry may have a better optimized economical balance for production

of transportation fuels and chemicals. Although many technologies for production of renewable transportation fuels and chemicals do exist there is a need for research and development to identify the most economic production processes. To achieve this it will be necessary to develop integrated processes with other industries e.g. integration of hydrogen production from BLG in a pulp mill with an ammonia plant.

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CHAPTER 7

Biomass conversion through torrefaction

Anders Nordin, Linda Pommer, Martin Nordwaeger & Ingemar Olofsson

7.1 INTRODUCTION

Torrefaction is a mild thermal pretreatment and refinement process presently attracting extensive interest and attention. Operating temperatures are between 200 and 350°C and it quite closely resembles the process of roasting coffee beans. Thereby the word torrefaction, which is simply French for roasting. The resulting torrefied biomass (Fig. 7.1) is an excellent solid energy carrier and product intermediate between biomass and charcoal, exhibiting several advantages in terms of improved inherent material characteristics. Table 7.1 is a compilation of both advantages typically claimed to be in favor of torrefaction and some aspects against or that need further development for torrefaction to gain commercial success.

Since the two “rediscovery-periods” of torrefaction 1984– (French work) and 2002– (Dutch work), scientists and engineers have gathered extensive experimental data on how different biomass raw materials may benefit from torrefaction. The process generally increases calorific value, water resistance, friability and grindability; and the product can be densified into pellets or briquettes for superior bulk energy density and eventually ground into powder for end-use. Biologic presence is terminated, reducing risk of degradation, spontaneous combustion as well as spreading of invasive and non-indigenous species. The final biomass fuel powder may also more resemble coal powder in terms of feed ability and process behavior, potentially facilitating biomass use in existing and new pulverized fuel conversion systems to a great extent. Ash related problems in the end-use processes might be significantly reduced by dedicated and intelligent fuel mixing and washing during the additional process stages, as well as by the potential chlorine separation during torrefaction.

Torrefaction is thus a biomass pretreatment process especially well-suited for employment early in the supply chain of biomass conversion systems to maximize the logistical, handling and system benefits. It may well significantly reduce milling, storage, transportation and other logistical costs; enhance biomass storage characteristics; reduce ash related end-use problems; facilitate extended international biomass trade and energy security; reduce climate impact from the whole



Figure 7.1. Original wood chips (left) and corresponding torrefied materials; light brown (center) and dark brown (right) subjected to 8 minutes at 260°C and 16.5 minutes at 285°C, respectively.

Table 7.1. Claimed torrefaction advantages and challenges.

Advantages	Challenges and important development areas
<i>Improved product characteristics</i> • Increased bulk energy densities combined with densification • Increased heating value • Reduced oxygen content • Dry and hydrophobic nature • Reduced biological presence • Reduced chlorine content • Increased friability, reducing grinding costs and particle size, increase of particle surface area • Increased quality and homogeneity • Cleaner burning fuel with less acid emissions <i>System benefits</i> • Refined fuel facilitating efficient gasification • Allowing higher co-firing ratios • Increased feed ability (after grinding) facilitating use of existing and new dry and wet feeding systems • Torrefaction plant full year heat sink for CHP integration	• Investment costs • Operating costs • Yield (energy loss) • Secure densified product yield and quality • Not yet commercially available • Storage issues – Leakage to recipient? – Smell and dust? • Neither processes nor product yet fully industrially proven

supply chain; facilitate cost-efficient large-scale biomass conversion systems; and accelerate the industrial development of refinement systems for biomass raw materials. Torrefaction will be useful both for fuel replacement in existing fossil fueled plants, and for new efficient conversion systems for biomass to a variety of valuable “green” products. The latter may be syngas production for heat and power or biomass to liquids production.

However, although several of the most important of the above advantages are well documented and many techno-economic advantages of torrefaction have been validated, there are still a few uncertainties around a few of the claimed advantages in Table 7.1. Claims also need to be fully validated in full-scale industrial use, i.e. after densification, transport and storage and when entering end-use transport, mills, burners and processes. Very few industrial full-scale tests have up till now been performed including the whole biomass supply and end-use processes. More economic estimations of whole supply chains are also needed. The present chapter will give some illustrations on, and a state-of-the-art summary of torrefaction, torrefied biomass materials, technologies suggested and the present status for the industrial and commercial development. A few estimates of the economy of torrefaction plants are also compiled.

7.2 TORREFACTION HISTORY

7.2.1 Origin of torrefaction processes

Torrefaction is a slow and low-temperature pyrolysis process not totally unlike the ancient coking piles for charcoal production used as reducing agent in early metal ore reduction processes, i.e. the backbone of the industrial revolution. The early technical development of the torrefaction process however started for coffee production in the late 1800s, as documented in the first patents (Thiel, 1897; Offrion, 1900). Quite a few more patents in the area of torrefaction can be found from the time periods 1922–1925 (>3), 1930–1932 (>3) and 1939–1952 (>10). Some research work on torrefaction dedicated to produce gasifier fuels was also performed during the 1930’s. During most part of the early and middle of the 20th century, only sporadic dedicated work on torrefaction for energy conversion were performed. However, more information and useful fundamental data

on heat treatment of lignocellulosic materials can be found from this time period in related areas of high temperature drying; dry distillation; thermal degradation; wood cooking; pyrolysis; heat stabilization and preservation of wood; (*c.f.* reviews by Beall and Eickner, 1970; Libra *et al.*, 2011; Esteves and Pereira, 2009).

7.2.2 Modern torrefaction work (1980–)

The modern work in the torrefaction area can basically be divided into; the initial French pioneer work documented by Armines (1981; 1982; 1985; 1986) and Bourgois *et al.* (*c.f.* 1984; 1988; 1989) during the years 1981–1989; and the recent extensive hype and efforts by a large number of groups initiated by the extensive and dedicated work by the scientists and engineers at Eindhoven University of Technology and the Dutch energy center ECN (*c.f.* Bergman *et al.*, 2005; Prins, 2005 and other reports reviewed by van der Stelt *et al.*, 2011). During the late eighties, the previous French work also resulted in a demonstration plant in France where torrefaction was used to produce a reducing agent for the metallurgic industry. The plant was erected by the company Pechiney and operated some years before it was dismantled for economic reasons. It should be mentioned and recognized that scientific work was also performed in parallel to the extensive French and Dutch work, *c.f.* Pentanunt (1990), Felfli *et al.* (1998a,b), Pach *et al.* (2002), Arcate (2002), Alen *et al.* (2002) and Lipinsky *et al.* (2002).

The recent and present efforts on torrefaction R&D are extensive with a large number of torrefaction R&D groups now working dedicatedly on torrefaction and the scientists and engineers are picking up speed also in terms of publications. The numbers of scientific papers on biomass torrefaction (and pyrolysis) during 2009–2011 as compiled in Web of Science were 11 (596) 2009, 9 (641) 2010 and 38 (739) in 2011. In addition, there are an even larger number of technical reports and conference proceedings published. However, the torrefaction reports are still below 5% of the produced material within biomass pyrolysis.

Surprisingly much effort has already been focused on compiling the present knowledge in several review papers, all with their own specific focus areas. Van der Stelt *et al.* (2011) for example, published a nice introduction to torrefaction, including a short history review and much of the characteristic data extensively gathered by the Dutch authors that thereby catalyzed modern torrefaction work. Tumuluru *et al.* (2011) wrote a summary of the torrefaction process, with focus on biomass constituents and their reactions (depolymerization, devolatilization and carbonization). The review by Chew and Doshi (2011) is an extensive compilation of biomass torrefaction data. Further, technologies proposed and used for torrefaction are to some extent compiled or illustrated by Walton and van Bommel (2011) and Kleinschmidt (2011). Ciolkosz and Wallas (2011) covered several different areas of interest in their review. The recent work performed within the Swedish torrefaction program was compiled by Pommer *et al.* (2012d). Additional torrefaction reviews are produced by Sun *et al.* (2012), Kargbo *et al.* (2009), and Kongkeaw and Patumsawad (2011). The closely related process of wood retification (preservation) by heat treatment at a somewhat lower temperature and longer time was reviewed by Esteves and Pereira (2009). Important issues of the effect of torrefaction on whole supply chain economics was recently compiled by Hawkins Wright (2012) and of importance of torrefaction for thermochemical conversion systems by Robbins *et al.* (2012).

7.3 TORREFACTION PROCESS

By heating the biomass to 200–350°C in an oxygen-deficient atmosphere for an appropriate time, many of the challenging properties of raw biomass materials are altered and the fuel quality will be significantly improved. The residence times initially suggested and studied were typically 0.5–2 hours, but it may be reduced significantly with a somewhat higher torrefaction temperature (280–350°C) if the process is carefully controlled in terms of initial moisture content, material residence time distribution and temperature. The Topell torbed torrefaction process could for example be

completed in less than two minutes at temperatures $<350^{\circ}\text{C}$ (Laughlin and Erasmus, 2009). Residence times of less than ten minutes have also been demonstrated suitable for chips of wood and logging debris of typical industrial thickness ($<10\text{ mm}$) in rotary kilns or screw conveying processes (Nordwaeger et al., 2013a,b). During torrefaction conditions, the biomass constituents will start to decompose and a small fraction of the biomass, enriched in oxygen volatilize and form a torrefaction gas containing different condensable and non-condensable species (Fig. 7.2).

The crucial parts of a torrefaction system include drying, torrefaction, cooling and subsequent densification for optimal product specifications. There are however, several interesting and quite different technical solutions presently suggested and evaluated by the many industrial initiatives working on developing torrefaction technologies (c.f. section 7.5). Although not completely valid for all of them, a schematic illustration of a “typical” torrefaction system is given in Figure 7.3, in which compulsory units are depicted darker.

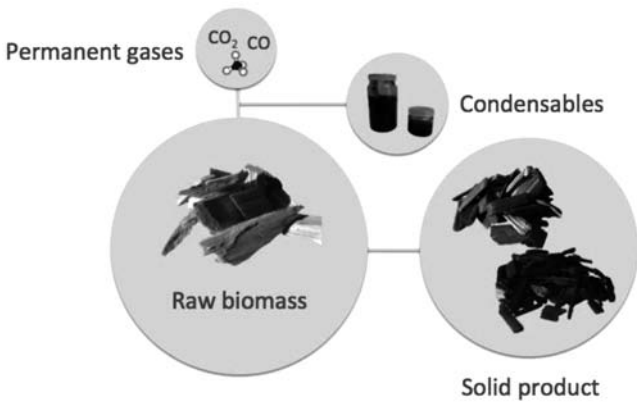


Figure 7.2. Distribution of torrefaction products. Depending on both biomass species and torrefaction process severity, the mass and energy distributions between the products may vary significantly. However, energy is always enriched in the solid product and very high yields are attainable ($>95\%$) still with most torrefaction benefits realized.

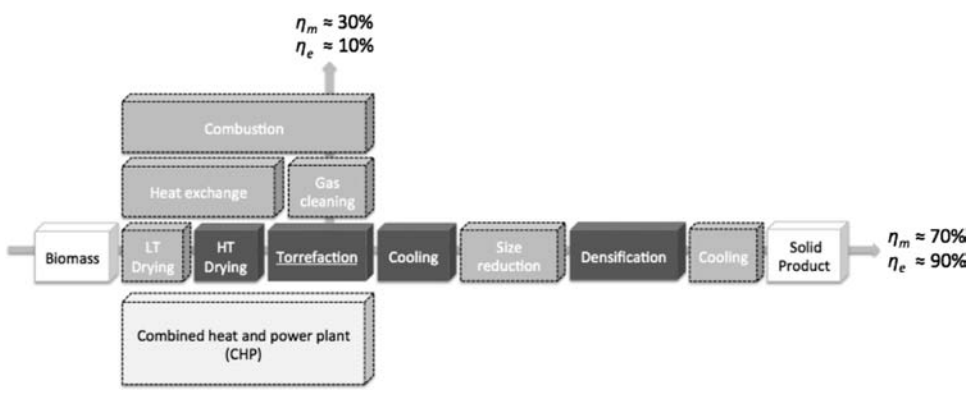


Figure 7.3. Illustration of the units of a typical biomass refinement plant/terminal, similar to most existing pellet production plants but here also incorporating a torrefaction process. Lighter gray units are optional, of which some potentially can be excluded for new torrefaction plants to reduce investment costs.

Initial drying before the torrefaction process is preferred to preserve the heating value of the torrefaction gas by avoiding too much dilution with water. For stand-alone processes, the heat for both the drying and torrefaction processes are typically generated from the chemical energy contained in the torrefaction gas via combustion. Instead of gas cleaning, the torrefaction gas and related equipment is typically maintained at a sufficiently high temperature to avoid condensation and extensive fouling. Torrefied biomass powder may by choice be used as auxiliary and startup fuel. Heat is preferably transferred utilizing hot (flue) gases and mixing chambers to reduce investment costs, but some kind of heat exchanger system may also be used. The torrefaction process may be either directly or indirectly heated, with the latter preferred for maximum value of the gas.

If possible, the high-value torrefaction gas should rather be used with more care. For torrefaction processes optimally integrated with power or chemicals production, the gas may for example be used for “green” products and residual heat is instead used for the drying and torrefaction processes. For good exergy performance, any available low temperature heat may be used in a low-temperature dryer prior to the high temperature dryer. Further, because of the friable nature of the torrefied material, the size reduction prior to densification may also potentially generally be excluded, but this has to our knowledge still not been evaluated.

7.3.1 Energy and mass balances

Torrefaction is characterized first of all by the calculated mass and energy balances, most often given as the mass and energy yields:

$$\eta_m = \left(\frac{m_{tor}}{m_{feed}} \right)_{daf} \quad \eta_E = \eta_m \left(\frac{HHV_{tor}}{HHV_{feed}} \right)_{daf} \quad (7.1)$$

where:

m_{tor} = mass of torrefied product

m_{feed} = mass of feed

HHV = higher heating value

daf = dry and ash free matter.

Typical values of 70% mass and 90% energy yields have often been used to illustrate the energy densification benefit of the torrefaction process, i.e. a significantly higher heating value is obtained. However, these typical given yields are not universally attainable. Compiled mass yields were for example reported by Chew and Doshi (2011) to vary between 24 and 95% and energy yields between 29 and 98% for different biomass raw materials experiencing varying temperatures (250–300°C) and residence times (30/60 minutes). Processes are typically operated at mass yields of 60–90% with the corresponding energy yields of 70–95%, implying a varying but still significant energy densification (Fig. 7.4). Recently determined ranges for wood materials and shorter residence times (4–25 minutes) and somewhat higher temperatures are 41–97% and 57–99%, for mass- and energy yields, respectively (Nordwaeger *et al.*, 2013a,b).

Parametric studies of two types of commonly used wood materials resulted in the response surfaces in Figure 7.5. Effects of temperature and residence time were generally of utmost importance for all studied responses time whereas the effects of N₂, steam and material thickness were typically found to be very low or non-significant.

7.3.2 Solid product characteristics

Torrefied biomass is typically light to dark brown, depending on the process conditions and black if severely torrefied. Many other properties of the raw biomass are also significantly changed when torrefied. Most of these changes are favorable for further processing of the torrefied product and to varying extent of profitable nature and described in more detail below.

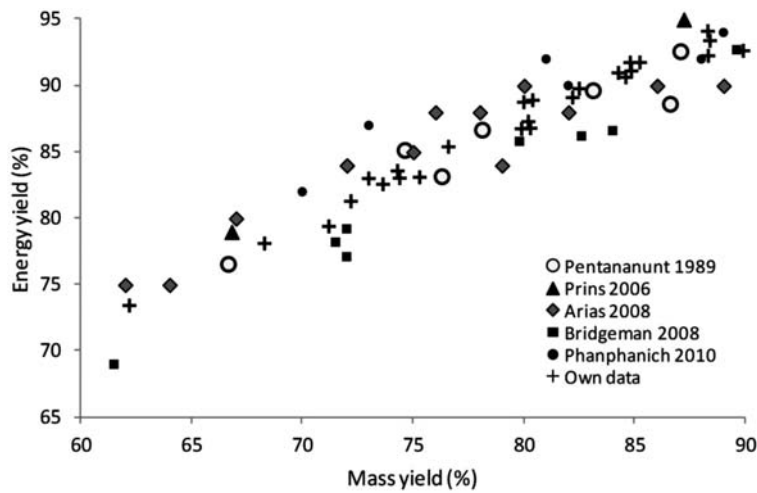


Figure 7.4. Compiled literature torrefaction data on energy and mass yields.

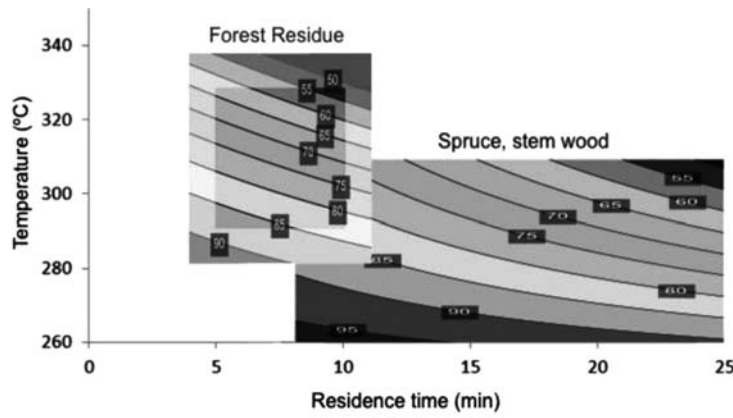


Figure 7.5. Effects of temperature and residence time on mass yield for torrefaction of wood residues and Norway spruce (Nordwaeger et al., 2013a).

7.3.2.1 Elemental compositional changes

The elemental changes of biomass materials when torrefied are quite extensive. A higher loss of oxygen and hydrogen compared to carbon leads to a relative increase in carbon content. To illustrate these typical changes, a Van Krevelen diagram (Fig. 7.6) is often used. Original dry biomass raw materials typically have H:C ratios of 1.4–1.6 and O:C ratios of 0.55–0.75 depending on biomass speciation. With increasing torrefaction severity, the chemical processes are basically accomplishing an “elemental dehydration” of the material finally representing the composition of coal and passing both those of peat and lignin. As previously described, the process is actually not a dehydration producing only water, but instead a large number of gas species enriched in O and H, resembling some kind of total elemental dehydration effect. To reach sub-bituminous and bituminous coal compositions, charcoal may be generated by pyrolysis, which is not the scope of the present chapter.

It should also be clearly noted that different biomass raw materials behave significantly different during torrefaction. Although the same type of torrefied material qualities may be obtained

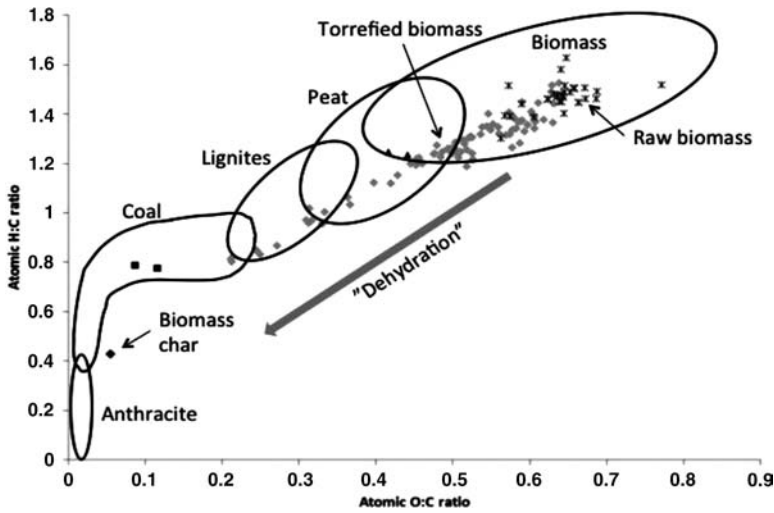


Figure 7.6. A Van Krevelen diagram illustrating the change in elemental composition of torrefied wood fuels (Nordwaeger *et al.*, 2013a,b; Olofsson *et al.*, 2013; Nordin, 1994).

by different biomass species, the specific temperatures, times and process cooling needed for different species may vary significantly.

No major changes in the content of nitrogen and ash-forming elements have so far been observed or reported in the literature except the anticipated specific enrichment due to loss of volatiles. At torrefaction conditions around and above 300°C however, a very interesting separation of chlorine has been reported by Örborg *et al.* (2013) and Norwaeger *et al.* (2013b) for two materials. If true also for more of the problematic fuels, it could be a substantial improvement of one of the more problematic issues of these raw materials. Alkali chloride induced deposit formation and corrosion have been extensively reported by both industry and scientific community. Torrefaction could potentially be a straightforward measure to disarm the alkali chlorides. A few studies have also reported the same type of trend for sulfur (*c.f.* Jafar and Ahmad, 2011).

7.3.2.2 Heating value and volatile content

The relative high loss of oxygen and enrichment of carbon in the solid product material results in significantly higher heating values of the product. They also vary extensively with the torrefaction conditions and reported data (Chew and Doshi, 2011) range between 16.4 and 26.4 MJ/kg. Compared to the original biomass, the increment of the *HHV* by torrefaction ranged from 1–58% for all the compiled data. The content of volatile matter also decreases during torrefaction. Volatile matter for the original wood types ranged between 80 and 88%, which by torrefaction was reduced by 1.5 to 35% of original values (Chew and Doshi, 2011). The effects of torrefaction temperature and residence time on lower heating value and volatile matter of spruce wood are illustrated in Figures 7.7 and 7.8, respectively (data extracted from Nordwaeger, 2013a). The effects of torrefaction temperature are generally larger than the effects of residence time but both show substantial impact on the torrefaction result.

7.3.2.3 Friability, grinding energy and powder characteristics

The typical fibrous and tenacious characteristics of untreated biomass are especially detrimental for applications in advanced pulverized energy conversion systems like co-firing with coal and biomass to liquid systems based on entrained flow gasification. The increased brittleness and friability of the material after torrefaction and the resulting final powder characteristics are

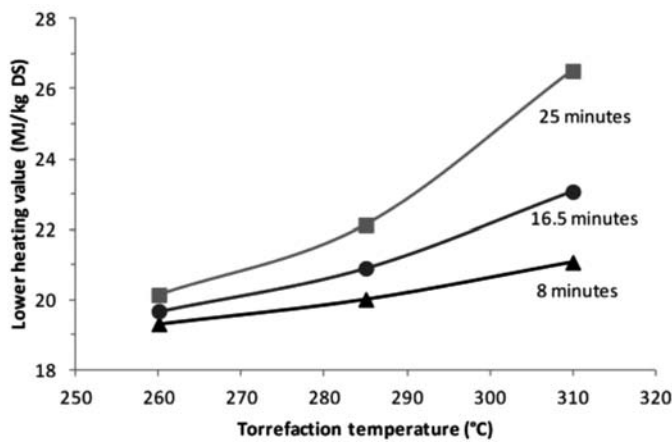


Figure 7.7. Lower heating value as function of torrefaction temperature and residence time for Norway spruce wood. Lower heating value of the original spruce wood was 19.1 MJ/kg.

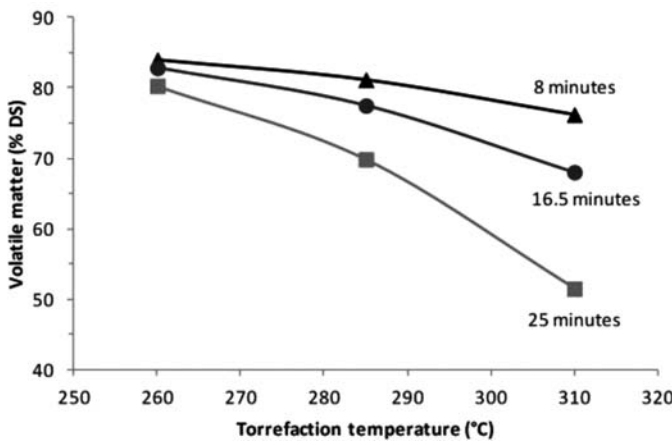


Figure 7.8. Volatile content as function of torrefaction temperature and residence time for Norway spruce wood. Volatile matter content of the original spruce wood was 85.4% of DS.

therefore of high interest. The friability in terms of increased production of fines and significantly lower grinding energies of torrefied biomass materials have been well documented for a large number of biomass materials and torrefaction conditions (as reviewed by Chew and Doshi, 2011; Tumuluru *et al.*, 2011 and van der Stelt *et al.*, 2011). Grinding energies are generally reduced by up to 90% depending on type of biomass and torrefaction severity. An illustration of the results from a recent study torrefying Norway spruce is given in Figure 7.9, where the energy savings were significant for the entire studied interval, ranging from 45% for the mildest treatment to 95% for the most severe torrefaction conditions (25 minutes at 310°C).

7.3.2.4 Feeding characteristics

The significantly changed physical properties and increased friability also highly influence the resulting powder characteristics after milling. Particle size distributions are changed to smaller particles sizes with increased sphericity and surface area, properties that are beneficial for both feeding systems and combustion and gasification processes behavior. Svoboda *et al.* (2009) wrote

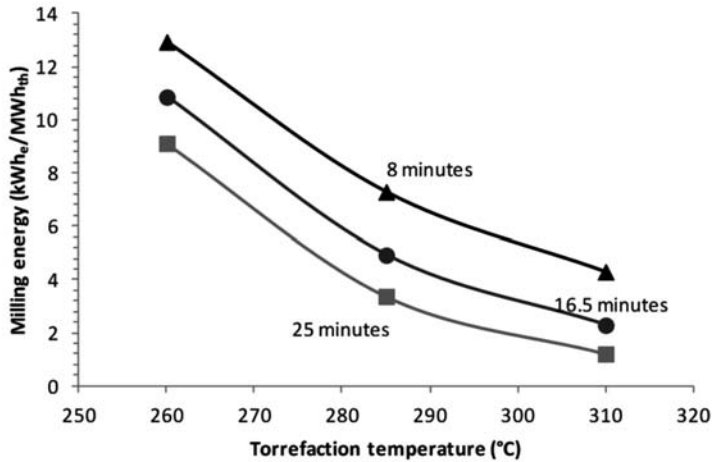


Figure 7.9. Quantified milling energies as functions of the main torrefaction process variables temperature and residence time. Corresponding milling energy for the raw spruce wood chips was determined to 24 kWh_e/MWh_t (data extracted from Nordwaeger, 2013a).



Figure 7.10. Illustration of the water resistance of torrefied (hydrophobic) material (right), compared to original (hydrophilic) wood chips (left) after one hour of exposure to water droplets.

a nice introduction to feeding challenges when utilizing biomass in entrained flow gasification (EFG). When evaluating the effects of different pretreatment processes on feed ability into the high pressure and temperature systems, they concluded that both torrefied powder and slurries based on torrefied material are promising ways of introducing the biomass into the processes. Further work is however needed to more carefully evaluate the different feeding related characteristics of resulting solid fluids, slurries and pastes of materials of different biomass origin and produced under different torrefaction conditions, and to perform real pilot- and full-scale tests of the different very interesting feeding options.

7.3.2.5 Hydrophobic properties and fungal durability

A number of studies have reported significantly improved water resistance for the torrefied materials produced, as illustrated for example by Figure 7.10.

Figure 7.11 is an illustration of both the increased water resistance (left axis) and the accompanying increased durability against fungi (right axis) of torrefied materials (Pommer *et al.*, 2013a). The raw reference material and torrefied products of varying torrefaction degrees were initially exposed for conditioning at 20°C and 65% relative humidity, ensuring theoretical wood equilibrium moisture content (EMC) of 12%. The resulting moisture content showed a distinct difference between torrefied and untreated samples. The EMC of the former being decreased to a half or less of the raw biomass, with typical EMC values of torrefied materials of about 2–5% in agreement with what previously reported (~3%) in the literature (*c.f.* van der Stelt *et al.*, 2011).

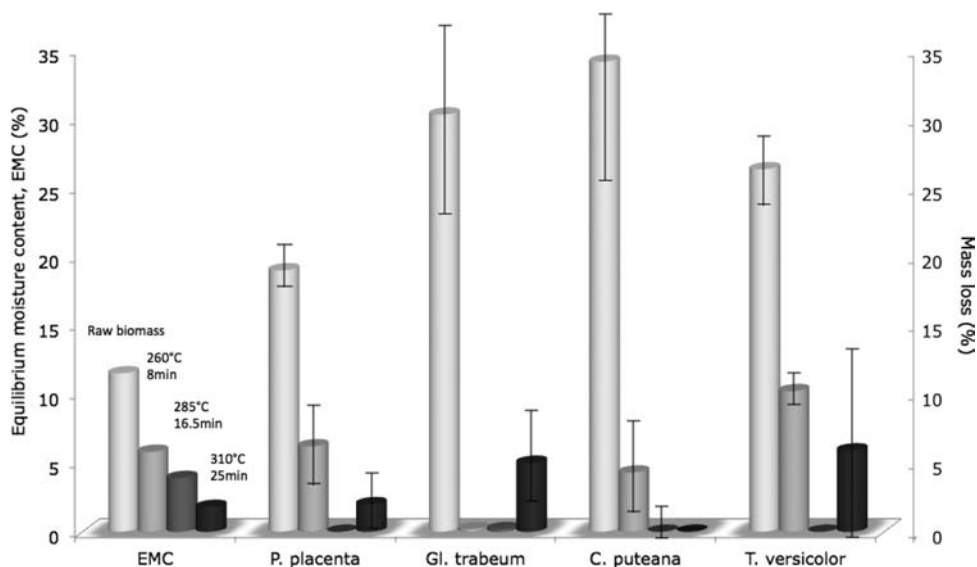


Figure 7.11. Equilibrium moisture content (EMC) of raw spruce wood and torrefied wood samples after exposure in 65% moisture at 20°C (left axis). To the right: Fungal durability against wood-destroying basidiomycetes, and corresponding for raw spruce wood and spruce wood treated in three different torrefaction severities (European Standard EN 113:1996, modified).

Concerning biological activity in general, relatively limited data have so far been published for torrefied biomass. In the above study, the different samples were also subjected to an accelerated fungal durability test. The results (Fig. 7.11, right axis) clearly showed that all thermally treated materials significantly improved the durability of the wood to a class 1, i.e. very durable when exposed to the tested fungi. The fungi were: *Postia placenta* FPRL 280; *Coniophora puteana* BAM Ebw. 15; *Trametes versicolor* CTB 863A; *Gloeophyllum trabeum* BAM Ebw. 109 (Pommer et al., 2013a).

Although a number of reports are available on the increased hydrophobic properties of the torrefied but not yet densified biomass materials, less information can be found on the actual densified form for transport and storage, i.e. for pellets and briquettes, especially the behavior in actual field tests. It is reasonable to assume that the surface of outgoing materials from the torrefaction process exhibit maximum water resistance, but if this material is grinded and densified, the new surface may give a somewhat different result. The data that is available on densified torrefied materials still indicate significant improvements compared to the original biomass. Bergman (2005) for example, exposed pellets of torrefied material to water by immersing them for 15 h, and reported only 7–20% water uptake and no disintegration, compared to the catastrophic behavior of the traditional pellets. Tumuluru et al. (2011) referred to their own previous report on 25% decreased moisture uptake of torrefied and pelletized material compared to the untreated control material. There are however also indications that the hydrophobic properties of densified materials are not as good as the torrefied biomass and may also vary depending on torrefaction and densification conditions. More work is therefore needed on actual full-scale field tests of the desired densified materials (from varying torrefaction conditions) under relevant conditions of repeated wetting (and freezing) over extended periods.

7.3.2.6 Molecular composition and changes

Lignocellulosic (“non-food”) biomass resources such as wood fuels, agricultural residues, dedicated energy crops are all composed of the polymers cellulose, hemicellulose and lignin

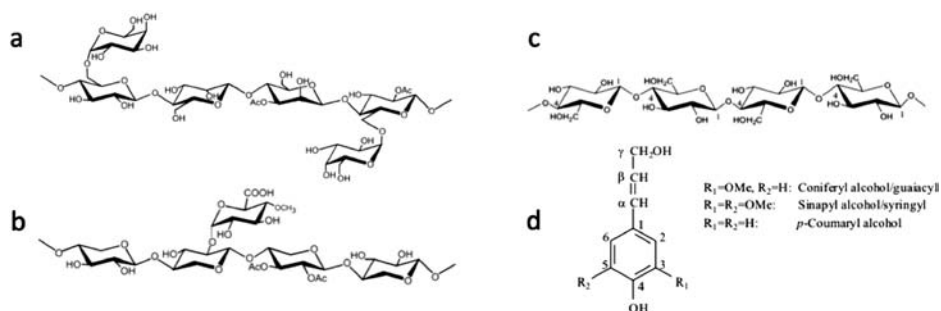


Figure 7.12. Schematic illustration of the main building blocks of lignocellulosic biomass: (a) galactoglucomannan (hemicellulose), (b) glucuronoxylan (hemicellulose), (c) glucose units (cellulose), (d) guaiacyl unit (lignin).

(Fig. 7.12). Spruce wood for example, typically consists of 40% cellulose, 31% hemicellulose and 27% lignin, with extractives making up the residual 2%. Torrefaction affects all these main components, but to a varying degree and in different specific temperature ranges.

A nice and in-depth work on the molecular transformations of the wood constituents during torrefaction was recently published by Melkior *et al.* (2012). Useful information can also be found in the literature on wood preservation by heat treatment (Weiland and Guyonnet, 2003) for the lower temperature range, and from pyrolysis work for the higher temperatures (Mohan *et al.*, 2006). In short, transformation/decomposition of the chemical wood components are suggested to be:

- cleavage of acetyl groups from hemicellulose, which induce depolymerization of the wood polysaccharides,
- dehydration reactions with the destruction of numerous hydroxyl groups,
- demethoxylation of lignin molecules yielding acetic acid, methanol and furfural,
- modification or disruption of the hydrogen bonding system in lignin and modification of linkages of lignin aromatic rings.

During initial heating exceeding 120°C, residual water linked to the macromolecules of the wood (mainly hemicellulose and cellulose) which requires an extra amount of energy to be evaporated is released from the biomass (Melkior *et al.*, 2012). When the temperature exceeds 200°C, CO₂ is identified as a result of biomass degradation and at 230°C, CO and methanol are identified (Melkior, 2012). In Pommer *et al.* (2013c), 15–20 different additional organic gases were identified already at 210–230°C. However, the extent of wood polymer degradation is very limited at these lower temperatures. An overview of thermal effects of the different wood components is presented in Figure 7.13. The decomposition temperature intervals (gray rectangles) for the different wood components are determined by thermo gravimetric studies (Grönli, 1996; Grönli *et al.*, 2002). Hemicellulose de-acetylation was clearly observed at 230°C for beech resulting in the formation of acetic acid (Melkior *et al.*, 2012), also supported by Pommer *et al.* (2013c) who identified acetic acid at >210°C for Norway spruce. A complete degradation of hemicellulose occurs at around 245°C. Amorphous cellulose may partly re-crystallize in the lower temperature region 200–245°C. Cellulose degradation starts at around 240°C and is complete at approximately 350°C. Small changes to lignin (demethoxylation or depolymerization) may occur at temperatures as low as 200–270°C but lignin degradation is limited at normal torrefaction temperatures (Melkior *et al.*, 2012).

The relatively higher temperature stability of cellulose and the degradation of hemicellulose are further supported by recent data on quantification of monosaccharide content in torrefied materials exposed to different torrefaction severities (Fig. 7.14). Glucose, the building block

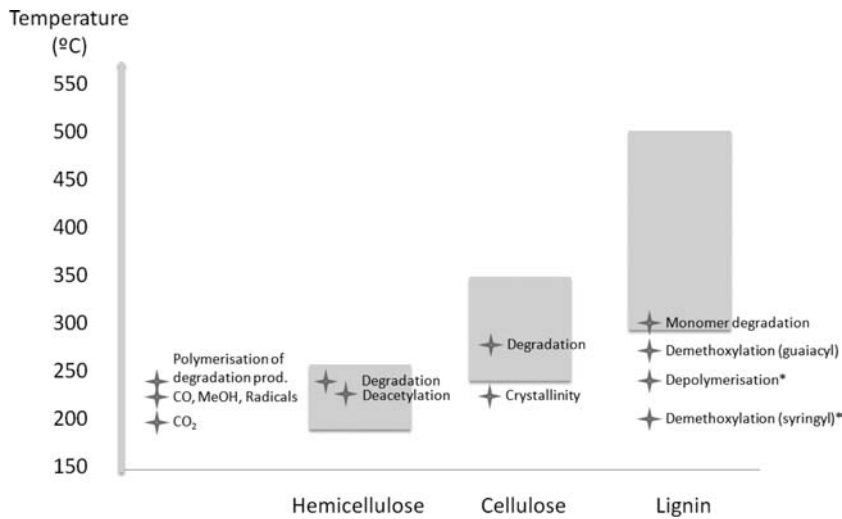


Figure 7.13. Overview of produced volatiles and transformation of the wood components as a function of the torrefaction temperature (from Melkior *et al.*, 2012; Gronli, 1996; Grönli *et al.*, 2002 and references in Mohan *et al.*, 2006). Stars indicate temperatures at which the chemical processes are clearly observed.

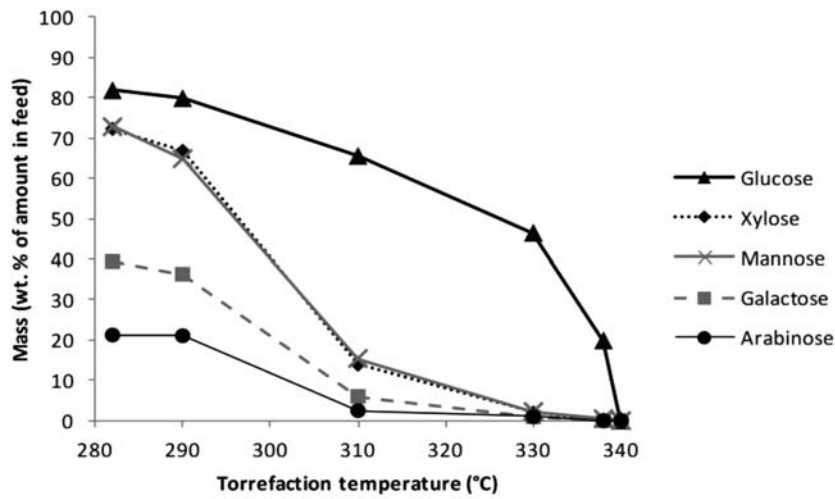


Figure 7.14. Quantified monosaccharide content in torrefied Norway spruce samples as function of torrefaction temperature (Data extracted from Nordwaeger *et al.*, 2013a).

of cellulose and part of hemicellulose is still remaining after moderate torrefaction conditions whereas mannose, xylose, galactose and arabinose constituting a large fraction of hemicellulose do not. At temperatures higher than 330°C however, not even the more stable glucose remains.

The amount of extractives in the biomass decrease by >10% during heat treatment at 260°C/15 min and continue to decrease at longer residence times according to Bourgois and Guyonnet (1988).

7.3.3 Gases produced

In a compilation of mass yields and the formed amounts of condensable and permanent gases from the literature, a clear obvious trend is that with increasing torrefaction severity, the amounts of formed condensable components and permanent gases increase. The higher the residence time during torrefaction, the higher is also the fraction of condensable formed (Prins *et al.*, 2006a; Ciolkosz *et al.*, 2011; Pommer *et al.*, 2013c).

7.3.3.1 Permanent gases

The permanent gases, also called incondensable gases, are gas species that remain gaseous under normal conditions and include e.g. CO₂, CO, CH₄, H₂, N₂, O₂ and a few organic components. The concentrations of the main components of the permanent gases, CO₂ and CO, increase with increased torrefaction severity and are formed in amounts of a few weight percent, with CO representing 10–30% of CO₂ levels depending on torrefaction settings and biomass types (Prins *et al.*, 2006a; Bourgois, 1988; Deng *et al.*, 2009; Ferro *et al.*, 2004; Pommer *et al.*, 2013b). At higher torrefaction severities, methane is also detected in low concentrations and the relative amounts of CO and CH₄ increase.

7.3.3.2 Condensable gases

Simplified, the condensable fraction consists primarily of water, acetic acid, methanol, furfural, hydroxyacetone and substituted phenols (Prins *et al.*, 2006b; Bergman *et al.*, 2005; Pommer *et al.*, 2013b). Water is formed by the dehydration reaction in hemicellulose, and acetic acid is formed by cleavage (thermolysis) of acetyl groups particular from hemicellulose (Boonstra, 2006; Bourgois and Guyonnet, 1988). The origin of methanol and furfural could, according to Melkior (2012), Weiland *et al.* (1998) and Weiland and Guyonnet (2003), be from demethoxylation of lignin.

At low torrefaction temperatures (<260°C) and short residence times (i.e. mass yields of >90%), only a few condensable gas components are volatilized from the biomass resulting from dehydration of the biomass and degradation of hemicellulose (Pommer, 2013b). Examples of components present at highest concentrations are: methanol, furfural, acetaldehyde, furan, and methyl acetate. Acetic acid was not detected for the lowest torrefaction severity. In Figure 7.15 the abundance of a selection of degradation components mainly from hemicellulose degradation are presented for different torrefaction severities.

Increasing the torrefaction severity (~270–290°C) results in a higher water content and significantly higher numbers of decomposition products, now resulting from all the three wood components: hemicellulose, cellulose and lignin. Some of the most common organic components in the torrefaction gas are acetic acid, water and hydroxyl acetone, acetic acid, water, methanol, furfural, butadiene, and acetaldehyde (Pommer *et al.*, 2013b).

At torrefaction temperatures of 300°C and above, components originating from the decomposition of lignin are more frequently found. The decomposition products from hemicellulose and cellulose are still present but are not the dominating components. Examples of the most common organic components in the torrefaction gas above 300°C are: acetic acid, water, hydroxyl acetone, dihydroconiferyl alcohol, eugenol, guaiacyl acetone, 1,4:3,6-Dianhydro- α -D-glucopyranose, isoeugenol, an unidentified anhydrosugar, ethylguaiacol, and guaiacol. At these more severe torrefaction conditions, both hemicellulose and cellulose and also lignin decompose to a larger extent thus forming phenol-containing components and larger polysaccharide decomposition products (Pommer *et al.*, 2013b).

Although the gas is a high value gas containing potential “green” chemicals and high value energy, the typical use is for combustion to generate heat for the drying and torrefaction processes. It is therefore of high interest to also calculate the heating value of the gas and ultimately the adiabatic flame temperature of the gas during heat generation. A sufficiently high adiabatic flame temperature is needed for efficient combustion and heat generation process. Because of the challenging organic load of the gas and the long residence time at around 300°C where polychlorinated organics potentially are formed, maximum efforts are needed to secure efficient

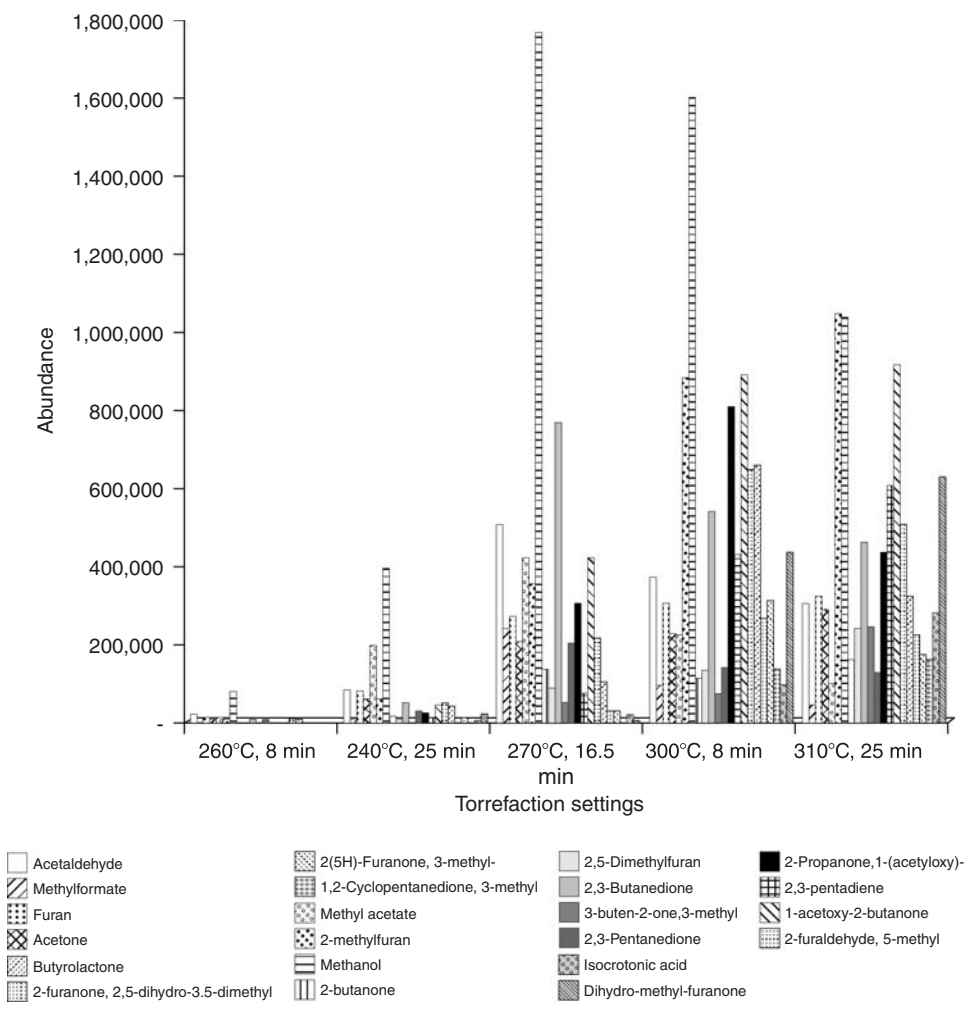


Figure 7.15. The abundance of a selection of decomposition products derived mainly from hemicellulose torrefying spruce wood at different torrefaction conditions.

combustion. This implies a sufficiently high gas heating value, sufficient refractory lining and residence time. A moisture content of maximum 10–15% can typically be allowed in the raw material entering the torrefaction process, still resulting in a gas with sufficient heating value for safe combustion. The exact critical moisture level is however significantly influenced by both torrefaction conditions and type of raw material used.

7.4 SUBSEQUENT REFINEMENT PROCESSES

7.4.1 Washing

Because of the hydrophobic characteristics of the torrefied material, it is alluring to introduce some kind of washing process for potentially separating ash-forming elements from the torrefied material. There are strong reasons to believe that a significant fraction of water-soluble elements



Figure 7.16. Torrefied and densified Norway spruce: briquettes (left) and pellets (right).

can be separated and the idea is thus exciting. Several initiatives have tried, but so far only limited results of these experiences have been published or industrially proven. Further validation for problematic biomass materials are needed, as are cost estimations in terms of increased investments; material losses to the leachate; handling of process water; and increased moisture in the product.

7.4.2 Densification

Maximum logistical and handling benefits of a torrefaction pretreatment process is not attained until the torrefied material is also compacted into a densified feedstock commodity (Fig. 7.16). This has traditionally been limited to pelleting, but other densification processes such as briquette presses, cube-makers, screw extruders, roller presses, tablet presses and agglomerators have been and are also still evaluated.

Bulk energy densities for pellets of torrefied materials are reported to be in the range 13–20 GJ/m³, at the best almost doubling the value of traditional pellets. Corresponding values for briquettes are somewhat lower and so are also the capacities of the briquetting machines. There are however, several other advantages with briquette production and several initiatives are therefore presently considering briquetting.

7.4.2.1 Pelleting

Initially, pelleting was pursued as the preferred densification method and most of the existing pilot and demonstration plants are equipped for pellets production. ECN early showed pelleting to be an interesting compaction method. Since then, many different biomass raw materials have been torrefied and pelletized at ECN (Gerhauser, 2008). Additional recent data from Norway spruce and Eucalyptus are added from Larsson *et al.* (2012) and Olofsson *et al.* (2013). The three Dutch industrial production plants in operation all installed pellet production lines in their plants. A number of studies utilizing laboratory-scale single pellet presses of different kinds (*c.f.* Stelte *et al.*, 2011) are also becoming available with useful fundamental information for mechanistic descriptions. Quite few field and full-scale studies with direct industrial value in terms of attainable energy densities, durability, hydrophobic properties and grinding costs have been published so far.

The expert groups in torrefaction process control and densification claim that pellet and briquette production is a quite straightforward effort, but also that a few tricks are helpful, as is careful process tuning and optimization. The general experiences from several torrefaction initiatives and industrial production units are on the other hand that pelleting of torrefied materials is associated with problems and severe challenges. The initiatives are presently struggling with

getting the pelleting to work efficiently in larger scale, especially concerning attaining the desired capacity and energy consumption. The issues reported include everything from severe problems in densification and binding characteristics (only limited production without binders), significantly increased friction and energy consumption for torrefied material to (fine tuning?) problems related to pellet quality like fines production or generation and durability challenges, as well as the quality assurance.

Our own experiences are limited to about 15 compaction trials and small projects, all with positive results in terms of success of compaction (some of them illustrated in Fig. 7.16), but also indicating increased friction and need for optimizing product quality, for example in terms of product durability. The few major initial findings are the following. Friction between compaction devices and biomass material is generally significantly increased by torrefaction, why devices with smaller press lengths therefore are used for torrefied materials, thus compensating for the increased friction energy. Water addition is and has previously been used as an additional degree of freedom in optimizing the densification processes. Temperature might also be used for optimization. Another important finding is that several initiatives, projects and authors have reported the deleterious pelleting behavior of severely (black) torrefied materials. As the torrefaction process is exothermal and generally challenging to control, many of the torrefied materials produced so far have most probably been over-torrefied, i.e. torrefied/pyrolyzed in a regime where also the lignin is attributed to significant changes and approaching charcoal quality. Both our own and ECN's experience seem to indicate that materials produced with sufficiently low torrefaction severity can (quite easily) be densified. There are reasons to believe that the compaction methods need a dedicated high quality torrefied material, for which torrefaction process control is crucial and that further optimization work including the combination of torrefaction and densification variables is desperately needed.

7.4.2.2 Briquetting

Briquetting torrefied biomass materials may soon be as interesting as pelleting. Size is flexible and might more closely resemble typical coal sizes and initial trials have been positive. Briquette production is typically more robust and possesses less wear, have higher availability and lower power consumption and operating costs in general. Maximum specific production capacity (per unit) is however somewhat lower, although development plans may be initiated to compete with the largest pelleting machines. The main question is whether sufficiently high bulk load in MJ/freight m^3 can be attained to be of interest for trans-continental shipment. Industry also needs to determine the optimal briquette size for best system performance. A smaller briquette size results in higher specific freight loads, but will also decrease production capacity and increase production cost. The optimal size of the briquettes needs to be identified and more data are needed on the system and hydrophobic behavior. Briquettes will most probably be interesting for industrial but not for residential use. For certain torrefaction plants and/or end-use sites, the present briquetting may already be more attractive than pelleting. Unfortunately, very few studies on briquetting of torrefied materials have been publically reported. However, Nielsen AS has been evaluating torrefied materials for briquetting in their systems with promising results. Briquetting thus looks promising and hopefully a briquetting press will be installed and demonstrated in the near future at a torrefaction production site.

7.5 TORREFACTION TECHNOLOGIES

7.5.1 General

During the last ten years, a tremendous torrefaction R&D activity from a large number of committed scientists and engineers combined with a genuine technology and business interest from many equipment suppliers and technology developers have resulted in a large and still increasing number of emerging torrefaction technologies.

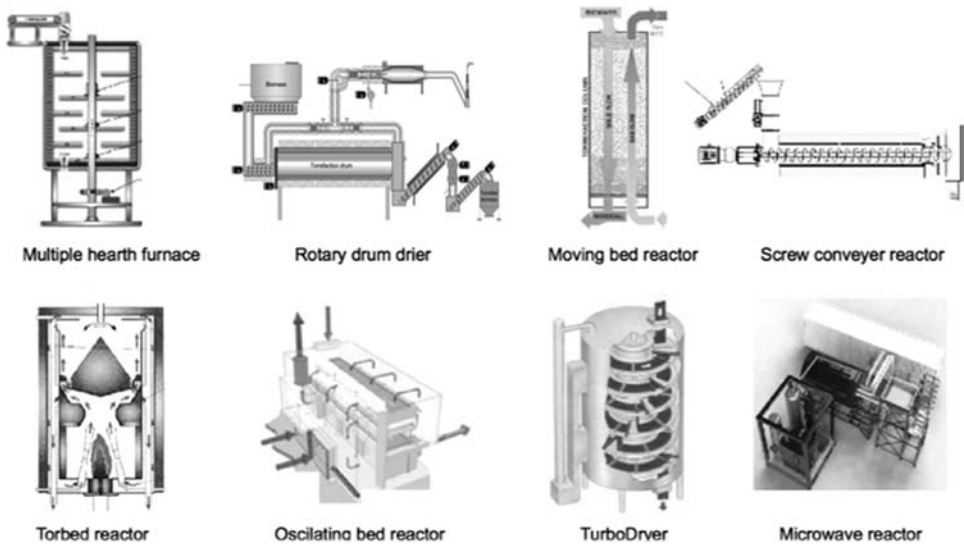


Figure 7.17. Illustration of some of the reactor technologies used for torrefaction (Kleinschmidt, 2011).

7.5.2 Technologies under development or demonstration

A very interesting aspect of torrefaction development is the large number of different reactor and system technologies evaluated and developed. Most of them are based on or developed from other existing technologies for drying or thermal conversion of biomass that now are refined for torrefaction purposes. Several of the different reactor types are illustrated in Figure 7.17 and a compilation of the different technologies was recently presented by Kleinschmidt (2011).

The technologies can basically be divided into directly or indirectly heated processes. Every reactor technology has its specific advantages and disadvantages and the overall efficiency also depends on heat integration design, in which a large number of options are possible. Independently of technology chosen, process control (residence time, temperature, particle size feed, mixing) is the key for good performance. Other important criteria are that technologies should be well-proven; robust; simple and cost-efficient; energy and exergy efficient; flexible to handle different raw materials; highly reliable with high availability; and allowing the production of a product with maximum yield as the raw material costs are the most significant single part of any cost analysis.

7.5.3 Status of the present production plants erected

Of all the 60+ claimed torrefaction initiatives and of all large-scale plants (15+) scheduled for start-up during 2010 and 2011, quite few are erected and hardly any has yet reached full stable industrial production and commercial status. The promises and thus expectations of start-up were initially set too high. Most suppliers tend to exaggerate their capacities and underestimate time and efforts needed. Developers with limited experience of biomass materials also found themselves struggling with “simple” challenges such as feeding, transport, storage and raw material quality. Another issue is the relatively high total costs. “Drying and drying some more” – it looked quite simple, attracting a hurdle of both serious developers and fortune hunters. However, it is a bit more complex than anticipated. Torrefaction has to be done intelligently, cost-efficiently and thoroughly for commercialization progress and success. Although not at all rocket science, there are actually a number of technical process and system challenges that need careful R&D and clever solutions such as: raw material handling; process containment and control of atmosphere; generation of inertization gas; heat transfer; moderation control of exothermal reactions;

product cooling; torrefaction gas behavior, fouling and utilization; process and system integration; energy and exergy optimization; densification; and whole supply chain optimization; but potentially most important process diagnostics and control. Because of the close relation between temperature and residence time and product quality and standardization, careful control of these process variables is crucial. The material produced should be completely homogeneous in terms of torrefaction degree and preferably dark brown (not overtorrefied) for a sufficient yield and to facilitate densification.

A few initiatives are hopefully paving the way for the torrefaction industry. There are presently four torrefaction demonstration plants up and running in Europe. Information is gathered from Internet, presentations on conferences and workshops as well as by personal visits. A nice update of present status of each initiative was also recently presented in the Hawkins-Wright report (2012):

- In Steenwijk, Netherlands, Stramproy Green in 2009 was the first supplier to erect a production plant with the first (45,000 t/year) of two lines commissioned 2010. It is thus designed for eventual production of 90,000 tonne/year and is also integrated with a 2.5 MW_e CHP plant. The original technology was an oscillating belt conveyor system but it was later redesigned to a fluidized bed based process. After a few issues on product specifications, a “false alarm” on emissions and a fire during 2011, production of commercial volumes is now expected. Stramproy started with pellets production, but have plans to produce briquettes.
- In Amel, Belgium, 4EnergyInvest is operating a torrefaction plant taken over from Stramproy Green. During 2011, the Amel plant has produced some 1000 tonnes and the first significant volume was delivered to a large-scale power plant to enable co-firing tests. The planned capacity is 40,000 tonne/year, but plant capacity is presently limited to 40% and the team is working on removing bottlenecks to reach full capacity mid-2012. In order to achieve adequate pellet durability, small amounts of starch are added as a binder.
- In Duiven, The Netherlands, Topell Energy and RWE Innogy GmbH are operating a commercial scale demonstration torrefaction plant of 60,000 tonne/year. It has completed its first phase of commissioning in excess of 1000 tonnes produced pellets and a continuous operating record in excess of 100 hours at rated output. Pellet quality is also here an issue, but they anticipate that binder-less pellets or briquette production will be possible.
- In Dielsen-Stokkem, Belgium, the Dutch company Torr-Coal Group erected a 35,000 tonne/year torrefaction plant 2009/2010 that has been in operation since October 2010. The initial focus was on solid recovered fuels, but now also covering wood chips and biomass in general. The production is in powder form, transported directly to an end-user for combustion but trial pellet production has also successfully been pursued.

At least seven more demonstration plants are scheduled for startup during 2012/13: BioLake (NL, 9 ktonne/year, 2012–), Thermya (Spain, 20 ktonne/year), ECN/Andritz (8–16 ktonne/year), FoxCoal (NL, 35 ktonne/year), EBES/Andritz (Austria, 8 ktonne/year), BioEndev (Sweden, 16 ktonne/year) Rotawave (Maine US, 100 ktonne/year). Some North America based initiatives with torrefaction processes are: Agri-Tech Producers, Integro Earth Fuels Inc., River Basin Energy, Torrsys and Wyssmont. In addition to the above larger demonstration plants, most developers have and are also operating pilot-plant processes based on their preferred technology.

7.6 END-USE EXPERIENCE

Although there is a tremendous interest in torrefaction and use of torrefied biomass materials, there is only limited information from actual full-scale tests in the open literature, in conference proceedings and workshop materials:

- A batch of 20 tonnes torrefied biomass was co-fired (9%) with coal at a 400 MW PC-fired plant in Borssele, The Netherlands in 2003 (Robbins *et al.*, 2012). The conclusions from the

trial were highly favorable. There was room to increase the percentage of torrefied wood in coal (i.e. the grinding mill limit was not reached), no decrease in conversion efficiency was detected and the fuel mixture showed good overall pulverization performance.

- The extensive field-testing of 4300 tonnes of steam explosion biomass in pellet form at the Vattenfall Reuter West plant in Berlin also validated most of the claimed advantages of heat-treated biomass materials. Vattenfall successfully handled and co-fired up to 50% SE pellets without any modifications of the plant. Issues reported were high COD values of leaching water from storage piles and increased dust generation during unloading. The latter was successfully handled by installing a simple dust suppression system.
- A significant volume of torrefied material was recently delivered from the 4EnergyInvest plant in Amel, Belgium to a power production plant for co-firing tests in a coal-fired power plant. The outcome of the tests was reported successful and no modification or investment was necessary to the power plant (Hawkins-Wright, 2012).

Conclusions are in general very positive but by scrutinizing the engineers in charge more carefully, there are also definitely areas of concern for further development. More and extensive field-tests and full supply chain analysis and evaluations are needed. The torrefied materials presently produced from the production plants in the Netherlands and Belgium are hopefully very soon carefully evaluated by industrial power plant owners and results openly shared with the rest of the progressing industry.

7.7 SYSTEM ANALYSES AND PROCESS INTEGRATION

7.7.1 Importance of total supply chain analysis

Torrefaction will most probably be an important integrated part of the complete supply chain of biomass for heat, power and “green” chemicals. For maximum logistic benefits, localization of most torrefaction plants should be as close as possible to the biomass feedstock. Some plants may also benefit from integration with other industrial and energy conversion processes and therefore located at these sites.

To fully explore the maximum energy/exergy and cost efficiency of biomass torrefaction, the entire fuel supply chain and site-specific systems must be considered, including logistics, scale and integration with other processes. Uslu *et al.* (2008) early concluded that the pre-treatment step has a significant influence on the performance of bioenergy chains. It affects all downstream processes and facilitates substantial improvements and cost reductions. Incorporating a pretreatment step will thus also significantly influence processes and routines upstream the torrefaction plant. Every combination of torrefaction plant and end-use customer will be unique and require their own supply chain sensitivity analysis. Models need to be developed that incorporate all parts of the biomass supply chain (*c.f.* Svanberg *et al.*, 2013) and process integration systems together with the torrefaction process in order to avoid sub-optimization (Håkansson, 2010) and gain maximum total efficiency in terms of economy and sustainability.

A torrefaction system is highly analogous to many of the present pellet production systems, both in terms of process unit operations and in a supply chain perspective as seen in Figure 7.18. There have thus been several comparisons of these two systems carried out, all strongly suggesting that the route *via* torrefaction (or retrofitting a pellet plant with torrefaction) renders significant benefits in terms of reduced total fuel costs and greenhouse gas reduction (see section 7.8).

7.7.2 Process and system integration

The torrefaction processes can be erected as stand-alone, low-cost and relatively small initial pretreatment plants close to the biomass resources. There are strong reasons to believe that existing pellet plants will be retrofitted with the torrefaction process. Torrefaction can also significantly benefit from different types of process and system integration, where for example the high-value

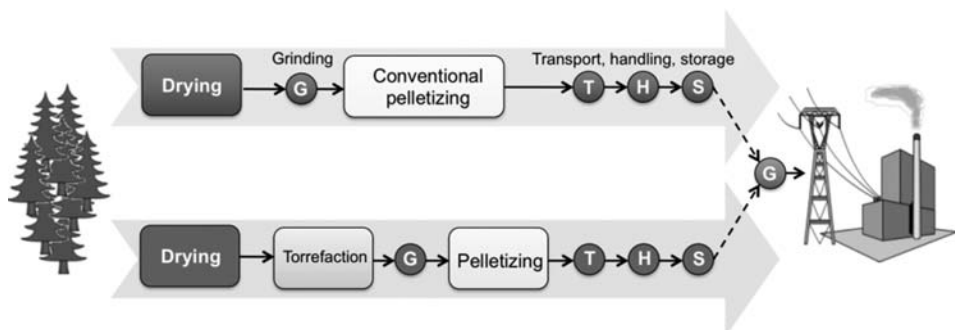


Figure 7.18. Illustration of presently dominating supply chain from biomass to end-use – based on traditional pellets (upper route) and the more logistically attractive route *via* introduction of a torrefaction process in the chain (below).

torrefaction gas is more efficiently used, and other low-value heat sources instead are used for drying and torrefaction. Ideally, an existing CHP plant situated in a biomass area is retrofitted with a complete torrefaction and densification system. New decentralized plants may also be considered for efficient co-generation of power on a relatively small scale. A number of different potential and interesting system designs including a torrefaction process are therefore foreseen:

- Mobile torrefaction units (to benefit from lower raw material costs);
- Standalone allothermal stationary units;
- Integrated with combined heat and power – existing or new plants;
- Retrofit of existing pellet plants;
- New (brown) pellet production plants;
- Brown pellet production with integrated new heat and power production;
- Integrated with existing industry, with excess low-value heat and/or use of a high value gas;
- Integrated with new biomass-to-liquids-production plants.

An illustration of results (Fig. 7.19) from models developed to simulate a few different degrees of integration with combined heat and power production was given by Håkansson *et al.* (2010) with the resulting thermal efficiencies compared to a stand-alone plant. Due to the inherent properties of the torrefaction process, it is well suited for energy integration with other processes where available low-value heat can be used for supplying the heat demand of the drying step. The model showed that when optimizing the total system, the thermal efficiency of the plant can be increased.

7.8 ECONOMIC ASPECTS OF TORREFACTION SYSTEMS

The potential economic feasibility of torrefaction pretreatment plants in the supply chain of biomass-based energy conversion systems has been estimated by several torrefaction initiatives and interests. A few techno-economic scientific papers can also be found in the open literature. It is however not a straightforward task, as the economic benefits stem from distributed effects of the whole supply-chain and also from within the production site and processes of the end-users. It is thus a challenging task for both scientists and industry and hopefully increased openness and the common interests will further encourage collaborative efforts to pursue refinements of the present models and estimations.

As pellet production, supply and use presently is the main and to some extent only established route from biomass to large-scale coal replacement, traditional pellet production plants and system are often used as analogy and/or reference. The following is a short compilation and illustration of some of the available information.

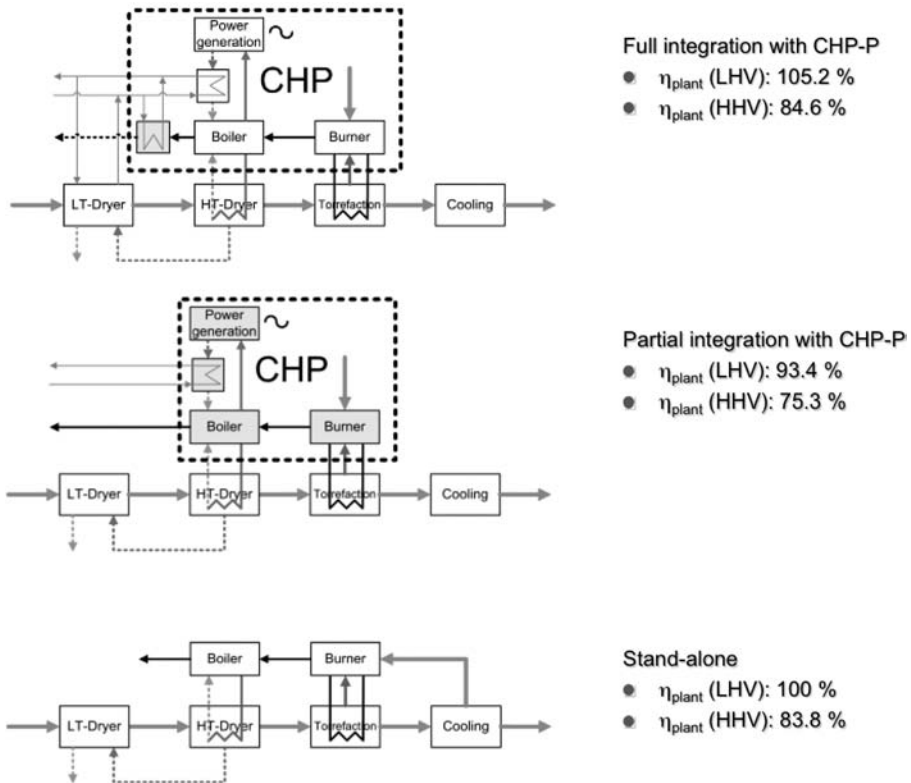


Figure 7.19. Illustration of a three different integration levels with CHP (Håkansson *et al.*, 2010).

7.8.1 Investment and operating costs

A typical investment costs for a complete commercial torrefaction plant is not presently available or easily estimated. The different technologies that are developed are of widely varying types and sophistication degree. All the operating and scheduled plants are also of a demonstration and first-of-a-kind type with significantly higher investment costs than for more mature plants. Recently performed feasibility studies further concludes that local site-specific conditions, coordinative savings, integration possibilities and investments may be significantly beneficial for the total economy.

All these specific conditions make every establishment unique in terms of benefits and costs. Extensive development work is also presently focused on reducing complexity and costs for the next generation plants.

Despite all this, the presently available investment costs for a number of erected and planned torrefaction plants (Fig. 7.20) and existing pellet production plants (Fig. 7.21) have been compiled for illustration purposes. The spread in data can be attributed to the immature market for torrefaction processes, different technologies and status of the initiatives, and last but not least what is actually included in the reported investment costs. It is however reasonable to assume that the upper broken trend line in Figure 7.20 represents a maximum cost for a complete stand-alone torrefaction plant of the present demonstration and first-of-a-kind type.

There are also strong reasons to assume that costs for the three plants following this line are all some 15–25% higher prized than typically anticipated at that depicted size. The facilities are designed and built for a larger commercial production capacity (double for two of them) than depicted in the figure and an extra 20% cost margin for engineering and other costs were

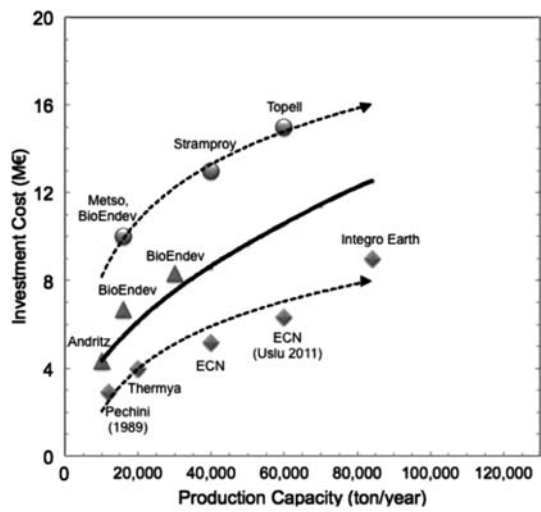


Figure 7.20. Gathered investment cost data *versus* annual production capacity for the present and planned torrefaction demonstration plants.

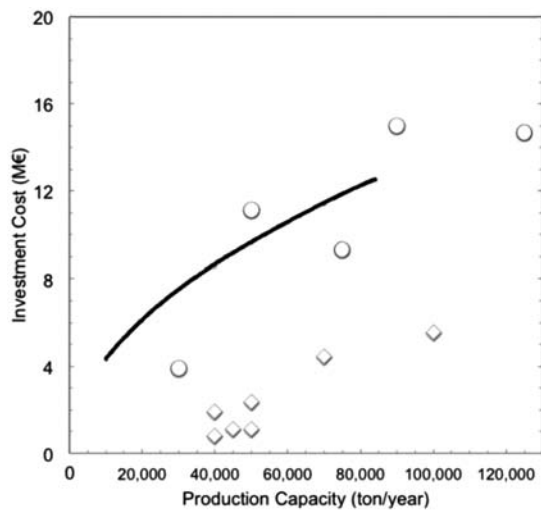


Figure 7.21. Gathered investment cost data for existing pellet production plants *versus* annual production capacity. Solid line is the same as in Figure 7.20.

included in the Metso/BioEndev project. The lower broken line includes plants for which only the torrefaction process is included and a few that are significantly cost minimized. The solid middle line follows a kx^α economy of scale relation with $\alpha = 0.5$, and may represent a rough but qualified estimate and potential target level for complete n th plants after significant and necessary cost reductions.

These values are also in line with five sophisticated and higher cost pellet production plants for raw biomass materials already in full commercial operation as illustrated in Figure 7.21. Several of

the lower cost pellet production plants are of less relevance here as they operate without dryer(s) or are utilizing existing infrastructure and integration in the original design. Based on these numbers and the expected development, it may thus be reasonable to believe that the investment cost for a stand-alone torrefaction plant in the near future could be expected to reach at least down to 10 M€ for a complete plant of 50 ktonne annual capacity and 13 M€ for an annual plate capacity of 100 ktonne. It could be argued that for a torrefaction plant in the same way as for pulp mills and car assembly factories, investments are only economically feasible in the largest scale. However, the costs for the initial transport of wet biomass raw material follow the opposite trend, thus implying an optimal distance and thereby also plant size, suggested to be larger than 80 or 100 ktonne/year (Uslu *et al.*, 2008; Svanberg *et al.*, 2013)). All these numbers are just estimates and need to be further validated and refined as the progress continues.

While capital costs of a typical torrefaction plant presently may be 25–30% higher than for a corresponding white pellet production plant, the estimated specific operating costs may be somewhat lower (Kiel, 2011). This is because of the improved characteristics of torrefied biomass materials; the increased friability reduces (or potentially avoids) size reduction costs prior to densification; the higher energy density increases specific energy throughput capacity in densification equipment. However, the often increased friction of torrefied material in the equipment may here be a significant challenge and needs further parametric and optimization studies. Slightly more feedstock is also required for a plant including torrefaction compared to a traditional pellet production plant. There is however still a lack of both fundamental and industrial data for any qualified estimates of operating costs, which is unfortunately generally true also for traditional pellet production plants.

7.8.2 Costs versus total supply chain savings

While torrefaction results in a significantly improved solid energy carrier, questions are still often raised as to whether or not torrefaction provides a net benefit to the biomass supply chain. Raw biomass chips may perform as well for local applications without the added processing costs but for longer transport and more advanced conversion systems, the benefits of refining the biomass have proven to be significant. Most presently available techno-economic supply chain studies have indicated that torrefied pellets can be delivered at the gate of a power plant to similar or lower cost per GJ than conventional pellets (*c.f.* van der Stelt *et al.*, 2011; Uslu *et al.*, 2008). Hawkins-Wright (2012) in their analysis of supply chain economics also recently concluded that torrefied and densified material can compete with traditional pellets.

The most extensive savings are however to be found within the gates of an end-user site. Handling and processing of traditional pellets require dedicated equipment e.g. storage/silos, biomass hammer mills, feeding systems and in some cases also burners. The required on-site investments are substantial as illustrated for example by Vattenfall (Fig. 7.22) and the savings of utilizing torrefied and densified materials instead of traditional pellets constitute 16% of total fuel costs for the utility. Corresponding savings as calculated and presented by Topell is 14%. Topell and investor RWE Innogy compared electricity production costs of co-firing torrefied pellets with solely coal combustion at the same coal plant. It was found that, in all cases, co-firing torrefied pellets is more cost-effective than co-firing conventional wood pellets and the majority of that cost advantage comes from avoided additional capital costs.

In a study by Zwart *et al.* (2006), the benefits of torrefaction and other pretreatment processes for production of liquids *via* EFG were evaluated and the different routes were compared. It was found that pretreatment significantly enhance the economic viability of synthetic fuel production and torrefaction was found to be the most attractive method.

The ultimate choice of torrefaction conditions for a specific biomass raw material will of course be a delicate tradeoff between maximizing energy yield and optimizing the total supply chain savings as a result of all other material characteristic changes. This trade off can be illustrated for energy yield and higher heating value in two dimensions but should ultimately include a composite cost model of the economic effects of all process, energy and material responses

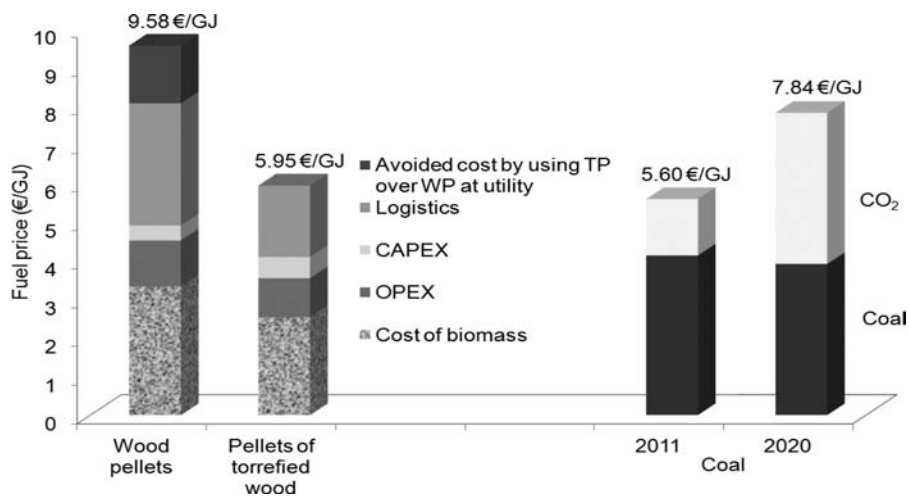


Figure 7.22. Comparison of fuel prizes for a coal fired plant (adapted from data presented by Vattenfall), UK co-firing subsidiary of 0.5 ROC is equivalent to 4.5 \$/GJ.

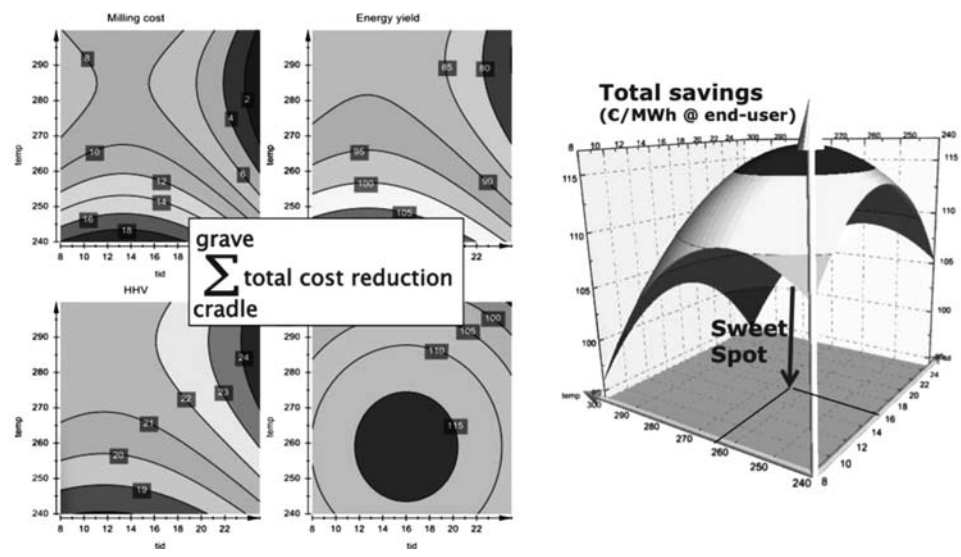


Figure 7.23. Each combination of torrefaction terminal, supply chain and end-user will most probably require its own torrefaction process optimization for its specific requirements on all different material characteristics.

for the whole supply chain. The trick is to identify the sweet spot (Fig. 7.23) for each specific combination of torrefaction terminal and end-user, including the whole supply chain (Nordwaeger et al., 2011).

7.9 OUTLOOK

Although torrefaction initially looked quite simple, the torrefaction initiatives are still struggling with technical challenges, product quality and cost reductions (Nordin, 2012). It is however

a creative and inspiring development atmosphere with immense R&D activities all around the globe combined with a large and increasing number of different and competing torrefaction technologies. We certainly will benefit from this flourishing and creative development atmosphere. Many technical challenges have already been solved and several smart solutions are presently demonstrated. Scientists and engineers are thus quite confident in the technologies and results obtained and feed on hope and excitement. However, we also need to be humble, patient and show respect for the ambitious task pursued.

Development normally takes time – generally 10–20 years for a new product or process to reach commercial success. Ten years have passed since torrefaction R&D was accelerated by the Dutch energy center ECN and the torrefaction industry may be quite close to picking up speed. Present torrefaction plants are approaching full productivity and several more are on their way. The hype and development will thus continue and huge global engineering and technology corporations Andritz, Metso and now also ConocoPhillips are picking up speed with impressive knowhow and recourses.

The competition is mostly against time and the low-cost fossil fuels. Although the economic studies already look quite interesting, the industry needs maximum efforts on all economic savings in the whole processes, systems and supply chains, i.e. a multitude of measures of different scientific and engineering nature. Torrefaction costs are still to be reduced, technology and quality improved and availability increased, but all these efforts are paving the way for commercial torrefaction. In the best of all worlds, the systems should also be based on well-proven and robust technologies, with minimal operational and investment costs, suitable also for up-scaling to hundreds of tonnes capacity. Thus, there are still some efforts in getting there. Key for the whole industry and the potential market penetration will be openness and humbleness in solving many of the remaining issues collectively. Hopefully, the year 2013 will (at last) result in several large-scale supply and end-use tests of industrially produced tonnages, critically evaluated, shared and used for further process and system refinements in the whole torrefaction industry.

The global demand for torrefied biomass is predicted by Hawkins-Wright (2012) to exceed 70 million tonnes per year by 2020. They further claim torrefied biomass is on the brink of becoming a viable feedstock for utility-scale electricity generators, potentially replacing coal, as well as some types of wood pellets. There are also strong reasons to believe that a drastically increased international trade with refined biomass fuels will balance the global biomass raw material prizes as biomass approaches a global commodity fuel.

An additional long-term aspect is that the co-firing may be a solution to the chicken and egg dilemma for production of “green” liquid fuels and chemicals. The coal replacement market is huge and already existing, significantly facilitating the market penetration of torrefaction systems. Dedicated biomass-to-liquids (BTL) systems can then be developed and demonstrated based on feedstock market and technologies already here for the coals. There are also reasons to believe that the major BTL challenges – feeding, ash behavior, total system efficiency and costs – can be significantly influenced by torrefaction and the initial results look promising. It is thus plausible that decentralized pretreatment (torrefaction) plants will be accompanied by larger centralized gasification and synthesis plants. However, still quite some time and R&D efforts remain, initially with focus on realizing the torrefaction industry.

It is the authors’ strong opinion that torrefaction has come to stay – although “the future looks dark”, a brighter day seems to be arriving for the biomass industry.

ACKNOWLEDGEMENTS

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CHAPTER 8

Biomass pyrolysis for energy and fuel production

Efthymios Kantarelis, Weihong Yang & Wlodzimierz Blasiak

8.1 INTRODUCTION

Pyrolysis is the thermochemical decomposition of organic matter in the absence of oxygen and produces a wide range of useful products. The word is coined from the Greek-derived elements pyr “πύρ-fire” and lysis “λύσις-breakdown/separation” emphasizing the disintegration of matter due to heat. It is a standalone process or one of several reaction steps in gasification and combustion processes¹ and is considered as the basic thermochemical process to produce valuable fuels and energy from biomass. Pyrolysis is also known as thermolysis, thermal cracking, dry distillation, destructive distillation, etc.; however, there are differences in those terms. During pyrolysis, complex macromolecules of biomass break down into relatively smaller molecules producing 3 major products which can be classified as follows:

- a solid residue (which mainly consists of carbon and ash) known as char
- gases (mainly CO, CO₂, CH₄, H₂ and other light hydrocarbons)
- Vapors/liquids known as bio-oil or bio-crude (mainly oxygenates, aromatics, water, products of low degree of polymerization, tars, etc.).

The pyrolysis process can be schematically represented by Figure 8.1. The quality² and relative proportion of the products depend on several factors such as temperature, heating rate, vapors residence time, pressure, biomass composition, etc. Pyrolysis generally starts at 300°C and continues up to 600–700°C – those limits are not absolute – leading to the formation of the above-mentioned products. Generally, lower process temperature and long vapor residence time favor char production, whereas high temperature and long vapor residence time increase the gas yield. Moderate temperature and short vapor residence time favor production of liquids (Bridgwater, 1994).

Based on the operating conditions, pyrolysis can be classified into three regimes/subclasses: (i) conventional or slow pyrolysis, (ii) intermediate pyrolysis, and (iii) fast/flash pyrolysis. Slow pyrolysis occurs under very slow heating rates (0.1–1°C/s) and very long residence time using large wood blocks as feedstock (Naik *et al.*, 2010). The major product is charcoal and it is also called carbonization (Bridgwater, 2012). Intermediate pyrolysis occurs at higher temperatures (300–700°C) at a fast heating rate, with residence time ranging from 10–30 s (Bridgwater, 2012). Fast pyrolysis occurs in a temperature range of 300–750°C, at a fast heating rate, and very short residence time (~1–2 s). In fast pyrolysis, biomass decomposes to generate vapors, aerosol, and some char. After condensation of vapors, a brown mobile liquid is obtained (bio-oil). Bio-oil production from biomass pyrolysis is typically carried out *via* fast pyrolysis. It has to be emphasized that the terms ‘fast’ and ‘slow’ pyrolysis are somewhat arbitrary and they cannot be

¹There is a limited number of authors who distinguish between pyrolysis and devolatilization. According to them, pyrolysis takes place in an inert or reducing environment and devolatilization in an oxidizing one (Lu, 2006).

²The term quality is arbitrary and according to ISO 9000:2005 refers to the degree to which inherent characteristics fulfill a requirement. In this text, quality refers to liquid fuel requirements.

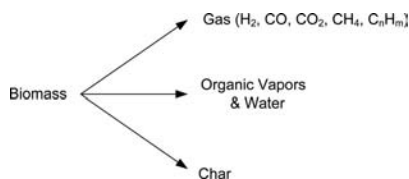


Figure 8.1. Overview of biomass pyrolysis products.

Table 8.1. Typical operating conditions and product yields for biomass pyrolysis.

Pyrolysis mode	Temperature [°C]	Vapors residence time	Liquid yield [%wt]	Gas yield [%wt]	Char yield [%wt]
Fast	500	1–2 s	60–75	13–20	12–20
Intermediate	500	5–30 s	40–50	25	25–30
Slow	400	hours-days	25–30	25–35	30–40

precisely defined (Mohan *et al.*, 2006). Typical product yields of different modes of biomass pyrolysis are shown in Table 8.1.

The heavy dependence of product distribution on operating parameters of pyrolysis is a result of the nature of the process, which can be described by the following steps (Mohan *et al.*, 2006):

- Heat transfer from a heat source, to the biomass (particle heating);
- The initiation of primary pyrolysis reactions and release of volatiles (mainly endothermic reactions);
- Flow of hot volatiles toward cooler solids which results in heat transfer between hot volatiles and cooler non-pyrolyzed biomass;
- Condensation of some of the volatiles in the cooler parts of particle, followed by secondary reactions (secondary cracking), that produce char;
- Autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions simultaneously occur in competition;
- Further thermal decomposition, recombination of radicals, can also occur, which depend on residence time, temperature and pressure profile.

The effect of cracking severity (temperature and residence time) can be understood by the pyrolysis path of carbohydrates described by Lange (2007) and shown in Figure 8.2. According to this pathway, at low temperature carbohydrates depolymerize resulting in formation of smaller units. At $\sim 300^\circ\text{C}$ dehydration reactions prevail, yielding unsaturated polymeric units and char. At higher temperatures C-C and C-H bonds cleavage is severe, producing smaller oxygenates and non-condensable gases (CO , CO_2 , H_2 , CH_4 etc.).

Pyrolysis has been applied for many centuries for charcoal production. Nevertheless it is only on the recent years that fast pyrolysis become of considerable interest, due to the fact that it can directly give high yields of liquids (up to 75 wt%) which can be used in a variety of applications (Czernik and Bridgwater, 2004). The nature of the process and high versatility of the products are expected to offer in the short-term sustainable exploitation of biomass resources (especially in remote areas), improved efficiency and environmental acceptability (Chiaramonti *et al.*, 2007). A simplified block diagram showing the process and product versatility can be seen in Figure 8.3.

The rest of the chapter addresses the most promising and emerging technologies of fast pyrolysis for bio-oil production, as well as bio-oil properties and applications for energy and fuel production. Finally, a brief description of kinetic modeling along with the recent research trends and developments in biomass pyrolysis is given.

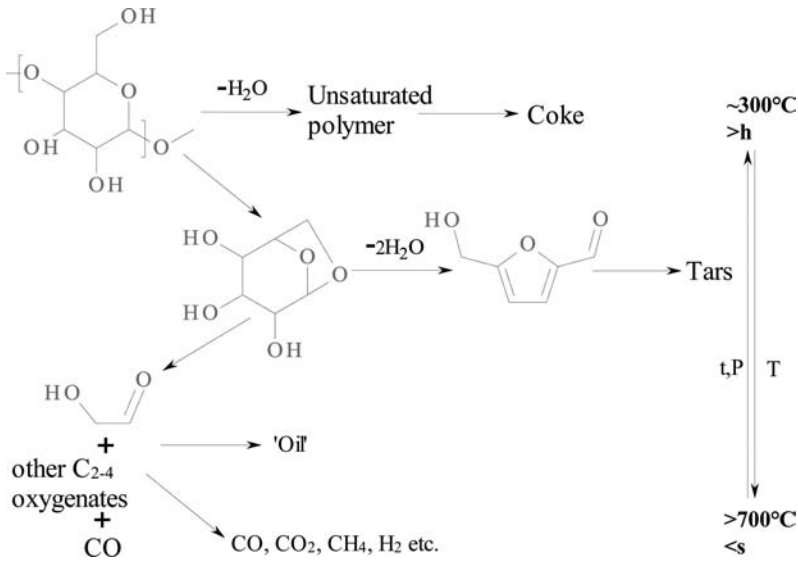


Figure 8.2. Pyrolysis of carbohydrates. Adapted from Lange (2007).

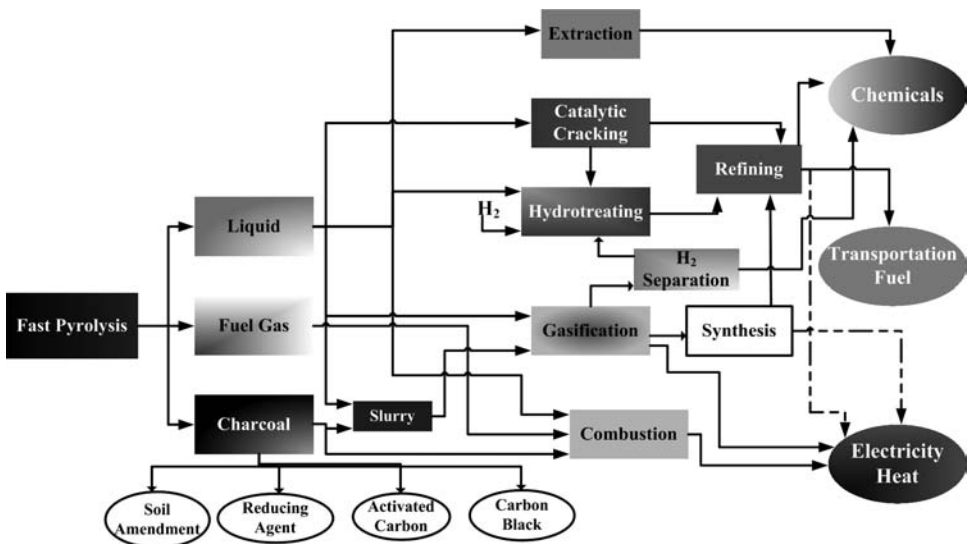


Figure 8.3. Fast pyrolysis process and product versatility.

8.2 TECHNOLOGIES

Fast pyrolysis is the most promising process for the production of fuel oil for power generation, production of fuels, chemicals and polymers (Demirbas, 2004; Chiaramonti *et al.*, 2007; Demirbas, 2001). Pyrolysis product (bio-oil) can be used in engines and turbines and also used as a feedstock for refineries for light fuels and/or chemicals production (Vamvuka, 2011; Divakara, 2010). However, for efficient bio-oil production, the biomass particles should be heated at very

high heating rates in a carefully controlled reactor temperature of around 500°C. Furthermore the residence time of the vapors in a high temperature environment should be limited to a few seconds. (Bridgwater and Peacocke, 2000). The above have implications on the technology selection and development (reactor and subsystems); generally processes comprise three main stages from biomass reception to delivery of one or more useful products.

8.2.1 Biomass reception and storage

Biomass handling systems analogous to the ones used in the pulp and paper industry are required (Bridgwater and Peacocke, 2000). Depending on the reactor technology and configuration some preparation such as drying and grinding may be needed. Size reduction is increasingly expensive as the particle size reduces and should be taken into account when considering the reactor configuration. For detailed information the reader could consult Amos (1998), Brammer and Bridgwater (1999), and Pang and Mujumdar (2010) among others.

8.2.2 Fast pyrolysis reactors

The heart of an efficient bio-oil production *via* fast pyrolysis is the reactor. The effect of reactor performance on the overall process economics should not be underestimated (Lerou and Ng, 1996), even though that normally represents a small proportion (5–15%) of the capital investment of an integrated system (Bridgwater, 2012; Dudukovic, 2010). For this reason considerable research and development effort has been put to improve the reactor's configuration with different biomass feedstocks. The limited number of large-scale applications to gain operational experience in conjunction with handling, storage and standardization issues imposes barriers to the development of a bio-oil market. Hence, many reactor technologies and configurations have been developed over the years in an attempt to produce bio-oil, but still there is no one to be considered as the best.

When considering fast pyrolysis processes one should refer to its governing principles mentioned above. Even though there is still activity on fixed bed systems, it is however highly unlikely to give high and adequate quality liquid yields especially at a commercial scale (Bridgwater, 2012).

A suitable reactor should meet 3 principles: (i) operation within the reaction engineering coordinates of temperature, pressure and residence time; (ii) should have a low risk of implementation; and (iii) can be scaled up to economically justified commercial size while maintaining the energy and mass balance efficiencies of bench and laboratory scale systems. In fact scaling up capability is a determining factor when considering a successful design of commercial processes (Krishna and Tie, 1994; Werther, 1992).

8.2.2.1 Bubbling fluidized beds

Bubbling fluidized bed (BFB) reactors are widely used in biomass fast pyrolysis. The reasons behind this are the well-understood technology and the long serving reliability in the chemical and petrochemical industry.

BFB reactors are characterized by high heat transfer rates with uniform bed temperatures, both being important attributes for fast pyrolysis. Effective heat transfer to biomass particles is achieved from the high hot solids density inside the bed. In most cases inert material such as silica sand is used as bed material; however there is an increasing interest for catalyst use. Typical heat transfer rates for bubbling fluidized beds are 200–550 W/m²K (Basu, 2006).

The residence time of the vapors can be controlled by selection of appropriate particle size of the bed material. The heating of the bed can be achieved in numerous ways such as introduction of hot fluidizing gas, submerged heating tubes/elements inside the bed, hot walls or hot sand (from a twin bed system) or injection of air/oxygen (partial oxidation reduces the liquid yield and quality). However, care should be taken about the heating method when scaling up.

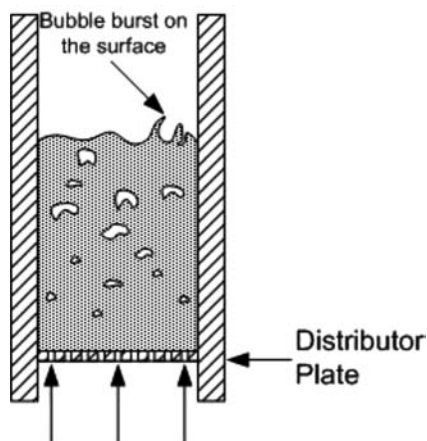


Figure 8.4. Bubbling fluidized bed.

An important aspect to achieve high heating rates and uniform temperature is the “quality” of fluidization (fluidization regime, particle size distribution of the bed material, etc.). Therefore, a carefully designed gas distributor is needed. A typical bubbling fluidized bed is presented in Figure 8.4.

Fast pyrolysis in a bubbling fluidized bed requires feedstock preparation. Generally, particle sizes less than 2–3 mm are required, with a maximum moisture content of around 10% (Bridgwater, 1999). The feedstock should be carefully sized and exhibit a narrow particle size distribution. If particles are too large, then the char after pyrolysis will be difficult to be entrained out of the reactor. On the other hand, if feedstock contains very fine particles, most of the biomass will be entrained out of the reactor without being completely pyrolyzed. In such cases, biomass should be introduced lower in the bed. Char accumulation on the top of the bed should be avoided since it enhances secondary cracking and results in lower liquid and higher char and gas yields.

Char production in BFBs is around 15% and accounts for 25% of the energy content of the raw biomass. Bubbling fluidized bed reactors can also be used in mobile applications, which can be advantageous in remote areas. Generally, BFB reactors are characterized by a relatively simple operating design and this type of reactor can be considered of being capable of conducting fast pyrolysis of biomass at commercial scale.

8.2.2.2 Circulating fluidized bed reactors

Circulating fluidized bed (CFB) reactors are quite similar to BFB except the char residence time is the same as for the vapor residence time. CFB reactors are suited for larger throughputs and they have more complicated hydrodynamics as compared with BFB. They are based on the riser type fluid catalytic cracking reactors (FCC) used for cracking of the residue of atmospheric distillation of crude oil; again hot solid and biomass mixing is crucial for optimum operation. Biomass fast pyrolysis in CFB can be benefitted by advanced mixing technology that has been developed through the years in petrochemical industry. Figure 8.5 depicts the mixing zone of Mobil’s commercial FCC Unit which could be used for biomass pyrolysis with some modifications (Hulet *et al.*, 2005; Chou and Lee, 1986).

Due to pneumatic transport, the biomass particle size should range between 1 and 2 mm. CFB reactors have limitations in the heat supply which is usually performed by recirculation of hot sand heated in a secondary char combustor. The use of a secondary char combustor implies that all of the char is used for heat generation and no or limited char is available for export unless a

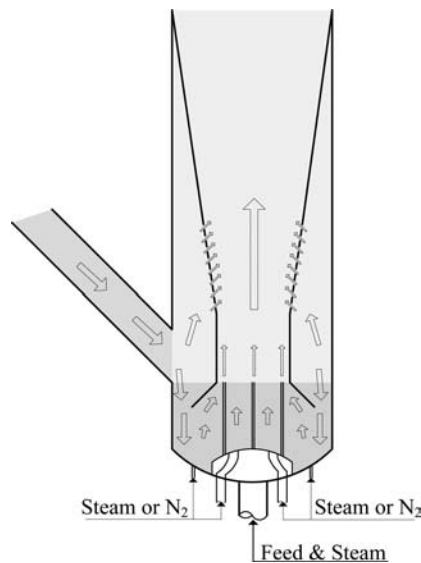


Figure 8.5. Mobil mixing zone (Chou *et al.*, 1986).



Figure 8.6. Ensyn's facility in Canada (Ensyn, 2012).

char separation section is used. Another major issue, which has to be proven during scaling up, is heat transfer.

Another disadvantage of CFB reactors is the fluidization gas requirements, which are higher than those in BFB reactors. Biomass pyrolysis in CFB has been successfully commercialized by Ensyn for food additives production (Ensyn, 2011). Ensyn's facility in Renfrew, Canada is shown in Figure 8.6.

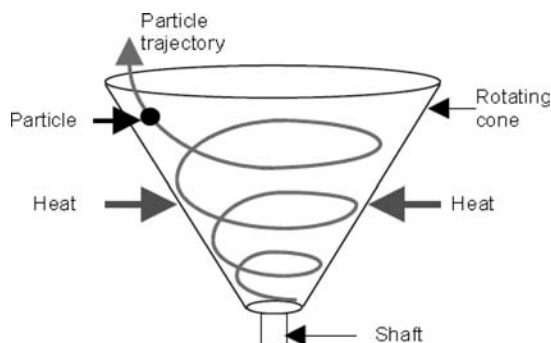


Figure 8.7. Operating principle of rotating cone reactor (Peacocke *et al.*, 2003).

Table 8.2. Overview of fast pyrolysis reactors (Pyrolysis Network, 2012).

	Status	Bio-oil yield	Complexity	Feed size specification	Gas requirements	Reactor size	Scale up	Gas quality
BFB	2–20 t/h	75%	Medium	High	High	Medium	Easy	Low
CFB	2–20 t/h	75%	High	High	High	Medium	Easy	Low
Rotating cone	0.2–2 t/h	70%	High	High	Low	Low	Medium	High
Entrained flow	1–20 kg/h	60%	Medium	High	High	Medium	Easy	Low
Ablative	1–20 kg/h	75%	High	Low	Low	Low	Difficult	High
Auger	20–200 kg/h	60%	Medium	Medium	Low	Low	Medium	High
Vacuum	–	60%	High	Low	Low	High	Difficult	Medium

8.2.2.3 Rotating cone reactors

Similar to the fluidized bed technology, where biomass comes in contact with a solid heat carrier, is the rotating cone reactor, which operates as a transported bed under the effect of centrifugal forces instead of a carrier gas.

According to the operating principle shown in Figure 8.7, centrifugal forces drive the hot sand upwards. Vapors are collected conventionally while char and sand are driven to a secondary fluidized bed reactor where the char is burned and hot sand is recirculated to the reactor.

As with CFB reactors char is burned to provide heat to the recirculated sand so it cannot be considered as product, unless char is separated and an alternative heating source is provided. Due to the very short residence time of biomass in the reactor, very fine biomass particles are required. This design is more complex for integrated operation while liquid yields of 60–70%wt can be obtained (Pyrolysis Network, 2012).

Several other configurations and designs have been proposed and used in laboratory and bench scale such as entrained flow reactors, ablative reactor, auger reactor etc. Details about those processes can be found elsewhere (e.g. Hulet *et al.*, 2005).

PyNe (Pyrolysis Network, 2012) has categorized the different reactor designs according to their characteristics as well as their commercial attractiveness and an overview is presented in Table 8.2. The close-coupled to the reactor downstream equipment (solid–vapor separation and liquid collection) should be carefully selected and designed because it will affect the bio-oil yield and nature/properties. The most important are the char–vapor separation and the liquid collection/condensation equipment.

8.2.3 Char separation

Char is normally separated by centrifugal gas–solid separation equipment such as cyclones. However, separation efficiency drops significantly for particles below 2–3 μm and inevitably, char fines are carried over and end up in the liquid. Downstream separation by liquid filtration is difficult due to rapid blockage of filters (Oasmaa and Peacocke, 2010).

Char acts as a catalyst and cracks produce vapors reducing the bio-oil yield by up to 20% (it also reduces the temperature at which maximum organic liquids are yielded) (Bridgwater, 2012). Char retains almost all of the alkali metals (Jendoubi *et al.*, 2011) which affect the yield and composition of obtained bio-oil. Potassium has been reported to be catalytically active during biomass pyrolysis yielding higher amounts of char (Nowakowski *et al.*, 2007). Phosphorus also gives rise to higher amounts of char while it changes the yielded products, indicating different pyrolytic mechanisms during decomposition (Nowakowski *et al.*, 2008). Agricultural waste usually contains a higher amount of ash (and alkali metals) than wood and hence char separation is of utmost importance.

Solid particles are also unwanted (in terms of particle size and total quantity) in demanding downstream applications such as combustion since it may block injection nozzles and create problems in stable operation of the process. Post-treatment of bio oil often involves a number of catalytic processes, each of which might suffer from poisoning of the catalyst by impurities such as alkali metals and compounds containing sulfur or nitrogen.

Metals present in bio-oil catalyze polymerization reactions, which result in gum formation and phase separation during storage. Hot vapor filtration can reduce the concentration of char and metals in bio-oil; however, filter clogging, pressure drop across filters and catalytic decomposition of pyrolysis vapors by cake filtration are limiting factors for their use (Wang, 2006). Hot gas filtration systems have been used both inside and outside the reactor (Wang, 2006; Kang *et al.*, 2006). Recently microfiltration has been used for removal of solid particles at submicron level (Javaid, 2010).

8.2.4 Liquid recovery

Once the char-free³ pyrolysis vapors leave the char-vapor separation system, they should be rapidly cooled to avoid secondary cracking that will reduce the yield and modify the chemical nature of the bio-oil. The configuration of the condensation system generally depends on the intended applications of the bio-oil product.

The rate of cooling is important. The use of conventional indirect (shell and tube) heat exchangers does not provide fast cooling resulting in lower liquid yields due to secondary cracking and differential condensation. The use of subzero cooled liquids to enhance the cooling rate should also be avoided because of the formation of agglomerated solid lumps (mainly composed of solids such as micro char) if bio-oil is cooled below 0°C (Choi *et al.*, 2012).

Even though differential condensation is desired for liquid fractionation and isolation of potentially valuable products for bio refinery applications (Chen *et al.*, 2010; Xu *et al.*, 2009; Ringer *et al.*, 2006), the selective collection of the lignin-derived components (highly viscous liquid) can lead to blockage of heat exchange equipment (Bridgwater, 1999). Due to the nature of the pyrolysis vapors (a form of mist/aerosol), capture is very inefficient by conventional cooling even if electrostatic precipitators are employed. Mist eliminators and coalescing filters are not practical due to rapid clogging of the small openings by very fine particles (Ringer *et al.*, 2006). Rapid cooling of the product is effective in a direct contact quench. Larger scale processing usually employs some type of direct contact with cooled liquid product that is effective (Zacher, 2009). Nevertheless, equipment must be designed carefully to avoid differential condensation of heavy ends that eventually lead to blockage of pipes

Spray scrubbing columns or packed bed scrubbers can be applied for maximum condensation in the minimum amount of collectors (Westerhof *et al.*, 2007). Venturi scrubbers have been proven

³There is no process to date that can produce 100% char-free vapors.

very effective; however, the added pressure drop to the system should be considered (Ringer *et al.*, 2006).

8.3 PRODUCTS AND APPLICATIONS

Fast pyrolysis is a zero waste process as the products, bio-oil and char, have commercial value (Pickell, 2003). Even though bio-oil is more of interest, bio char is also a useful byproduct that adds value to any fast pyrolysis venture.

8.3.1 Char

Char is the other major pyrolysis product (~15%wt and 25% of initial biomass energy content). It contains inorganic materials and unconverted organic solids and carbonaceous residues and is produced mainly from lignin decomposition

Char from fast pyrolysis is very flammable (auto ignition temperature between 200 and 250°C) which is similar to powdered coal. The ash content of the char is about 6–8 times greater than in the original feed and its alkali content is high which may cause problems in combustion applications. High-pressure pyrolysis leads to a higher charcoal yield of higher heating value (Antal *et al.*, 2000; Mahinpey *et al.*, 2009).

Char can be used as a heat supply for the pyrolysis process and in some metallurgical processes as a substitute for coke (Briens *et al.*, 2008). Char from pyrolysis can also be used as a fertilizer alone or mixed with soil and sand (*black earth*: 70% char: 30% soil and sand) providing recycling of valuable minerals to the soil, which is of huge importance for sustainable biomass use and industrial agriculture (Hornung *et al.*, 2011). Char improves the soil texture while slowly enriching it by releasing the retained nutrients and water; furthermore it acts as a support for organisms (Briens *et al.*, 2008). Char from biomass pyrolysis can also be used for activated carbon production increasing the added value of the material (Ioannidou and Zabaniotou, 2007).

8.3.2 Bio-oil

8.3.2.1 Composition and properties

The liquid product of biomass pyrolysis is the most attractive for commercial use due to its increased energy density, ease of transportation/use and de-coupling of production and utilization processes (Bridgwater, 1994).

Bio-oil is a complex multi-component mixture of molecules derived from depolymerization and fragmentation of biomass building blocks, namely: *cellulose*, *hemicellulose* and *lignin*. It can be classified into the following generalized categories: hydroxyaldehydes, hydroxyketones, sugars and dehydrosugars, carboxylic acids, and phenolic compounds (Piskorz, 1988).

Cellulose contributes mainly to bio-oil production and its decomposition produces anhydro-cellulose and levoglucosan. *Hemicellulose* decomposes to more volatiles and char, and less tar, while most of the acetic acid produced during pyrolysis comes from hemicellulose. *Lignin* decomposition produces bio-oil with lower oxygen content and therefore a higher energy density; however it is more difficult to be cracked and its products are characterized by high viscosity (Butler *et al.*, 2011; Oasmaa *et al.*, 2009; Shen *et al.*, 2010; Nowakowski *et al.*, 2010).

The complex chemical nature of the bio oil requires several analytical techniques for complete chemical characterization. Around 40%wt of the bio-oil contains compounds which are GC-MS (Gas Chromatography-Mass Spectrometry) detectable and 15–20%wt non-volatile compounds which are HPLC (High Performance Liquid Chromatography) detectable. However there is around 15%wt of bio-oil that is still undetectable, comprising of high molecular weight compounds. Several techniques such as Gel Permeation Chromatography (GPC) (Garcia-Perez *et al.*, 2007), Fourier Transform Infrared Spectroscopy (FTIR) (Özcimen and Mericboyu, 2010) have been

Table 8.3. Common chemical groups in bio-oil. Adapted from Bridgwater (2005).

Chemical group	Number of compounds identified
Acids	12
Sugars	8
Aldehydes	5
Esters	1
Alcohols	4
Ketones	32
Phenolics	56
Oxygenates	16
Hydrocarbons	6
Steroids	15

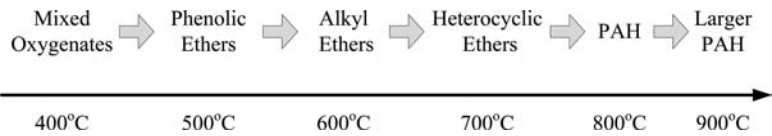


Figure 8.8. General pathway for liquid product chemical functional degradation. Adapted from Elliot (1986; 1988).

used in order to determine the bio-oil composition. Some of the common chemical groups of the compounds that have been reported to be present in bio-oil are shown in Table 8.3.

The chemical composition of bio-oil is important because it gives insights into its properties and suitability for downstream upgrading/processing, handling etc. The major difference from petroleum-derived fuels lies in the oxygenated (aliphatic and aromatic) compounds.⁴ Their relative proportion and class in the final product depends on the cracking severity and type (thermal or catalytic). A general pathway of the compound classes as a function of temperature is given by (Elliot, 1986) and is described in Figure 8.8.

Pyrolysis is not a thermodynamic equilibrium process and consequently bio-oil will have a non-equilibrium composition. This means that bio-oil tends to reach thermodynamic equilibrium during storage (Zhang *et al.*, 2007) and changes its composition and properties. These properties are (directly or indirectly) related to its oxygen content. The oxygen content in bio-oil is usually greater than 35% in more than 300 different compounds (Zhang *et al.*, 2007). Furthermore, bio-oil contains a considerable amount of water, which can cause phase separation and handling problems if it exceeds a threshold (Oasmaa and Peacocke, 2010). The water comes from the feedstock moisture as well as from dehydration reactions during decomposition (mainly from cellulose and hemicelluloses). A summary of typical properties of bio oil is listed in Table 8.4.

8.3.2.1.1 Homogeneity

In general, most bio-oils are homogeneous in appearance. However if biomass contains substantial amounts of extractives it will separate into two phases. The top phase is rich in extractives and the bottom phase resembles normal bio-oil (Oasmaa *et al.*, 2003). Most of the raw biomass materials contain a few extractives and they do not exhibit phase separation, because extractives are dispersed in the bio-oil matrix. Although most bio-oil can be macroscopically characterized

⁴As compared to petroleum, bio-oil also contains less sulfur, but may contain more nitrogen and chlorine.

Table 8.4. Typical properties of bio-oil. Adapted from Oasmaa and Peacocke (2010).

Property	Range (Wet basis)
Density (at 15°C) [kg/L]	1.11–1.3
Lower heating value [MJ/kg]	13–18
Kinematic viscosity (at 40°C) [cSt]	15–40
Thermal conductivity [W/m K]	0.35–0.43
Specific heat capacity (at 25–60°C) [J/gK]	2.6–3.8
Pour point [°C]	1–36
Coke residue [wt%]	14–23
Flash point [°C]	40–110
Ignition limit [°C]	110–120
Ignition temperature [°C]	600–700
Water [wt%]	20–30
Solids [wt%]	<1
Vapor pressure (at 33.5°C) [kPa]	5.2
Surface tension [mN/m]	29
C [wt%] (dry)	50–60
H [wt%] (dry)	6–7
N [wt%] (dry)	<0.4
O [wt%] (dry)	35–40
S [ppm]	<500
Cl [ppm]	<75
Ash [wt%]	<0.3
pH	2–3
K and Na [ppm]	<500

as a single phase liquid, it has been reported that it is actually microscopic multiphase structures or micro emulsions (Radlein, 2002).

8.3.2.1.2 Water content

The presence of water has both negative and positive effects on the oil properties. It lowers its heating value, especially the *LHV* and flame temperature. It also contributes to the increase in ignition delay and in some cases to the decrease of combustion rate compared to diesel fuels. On the other hand, it improves bio-oil flow characteristics (reduces the oil viscosity), which is beneficial for combustion (pumping and atomization). It also leads to a more uniform temperature profile in the cylinder of a diesel engine and to lower NO_x emissions (Elliot, 1994). The $-\text{OH}$ radicals generated in combustion from water reduce the soot formation and accelerate its oxidation (Calabria *et al.*, 2007).

8.3.2.1.3 Viscosity/rheological properties

Viscosity is an important fuel property to be taken into consideration when designing pumping systems and practical application of bio-oil as fuel. In general, bio-oil has high viscosity as compared with crude oil and diesel fuel; however, its viscosity is very similar to that of crude oil in a temperature range of 35–45°C. Viscosity of the bio-oil is related to fatty acid chain length and number of saturated bonds (Sensöz and Kaynar, 2006).

Rheological property of bio-oil can be described by the following equation:

$$\tau = \tau_0 + \mu D^n \quad (8.1)$$

where τ is the shear stress, τ_0 is the yield stress, D is the shear rate and n is the power law index which determines fluid's behavior. Extensive studies on rheological characterization of several bio-oils from wood have shown that bio-oils exhibit an essentially Newtonian behavior at the

shear rate range of 1 to 1000/s ($\tau_0 = 0$, $n = 1$) (Leroy *et al.*, 1988). However, some bio-oils rich in extractives may exhibit non-Newtonian fluid behavior (Lu *et al.*, 2009).

Generally, high viscosity fuel may result in poor atomization and incomplete combustion, coke deposition on injection nozzles and the combustion chamber. Moreover, the viscosity of the fuel directly influences the mixing in the combustion chamber.

8.3.2.1.4 Acidity

Bio-oil contains a considerable amount of carboxylic acids, which reduce its *pH* value to 2–3 and Total Acid Number (TAN) ranges between 50 to 100 mg KOH/g (Zhang *et al.*, 2007; Li *et al.*, 2008). Thus, bio-oil can be characterized by high corrosiveness especially to carbon steel, cast iron at temperatures above 45°C, mild steel, aluminum, copper (Aubin and Roy, 1990; Fuleki, 1999; Darmstadt *et al.*, 2004). Suitable materials for bio-oil storage and transportation include stainless steel, cobalt materials and various polymers such as polyethylene, polypropylene and polyester resins.

The acidity of fast pyrolysis bio-oil is derived mainly (60–70%) from the volatile acids while the acidity of the “sugar” fraction, covers around 20% of the total acidity mainly because of hydroxy acids (Oasmaa *et al.*, 2010).

8.3.2.1.5 Heating value

The heating value is affected by the oxygen content of the bio-oil and is about half of petroleum fuels. The heating value can be measured using a bomb calorimeter; however, a useful correlation for higher heating value determination from elemental analysis of the bio-oil has been proposed by Beckman *et al.* (1990):

$$HHV = 0.352(\%C) + 0.944(\%H) + 0.105[(\%S - (\%O))] \quad [\text{MJ/kg}] \quad (8.2)$$

where (%X) is the wt% of the corresponding element (C, H, S, O).

The lower heating value of the bio-oil can be correlated to its *HHV* by the following equation (Oasmaa *et al.*, 1997):

$$LHV = HHV - 218.3(\%H) \quad [\text{kJ/kg}] \quad (8.3)$$

8.3.2.1.6 Stability

One of the most important effects on the bio-oil is the effect of time on its physical properties and especially on viscosity and homogeneity of the sample. Those effects are important if the bio-oil is used in combustion applications (Peacocke *et al.*, 1994). The main effect of time is the increase of bio-oil viscosity due to polymerization reactions taking place even at storage conditions (there is evidence of reaction between bio-oil and oxygen from air).

The ash content is one of the most important parameters in the bio-oil stability. It has been reported that the ash content in bio-oil should not exceed 3% wt in order to avoid phase separation during aging (Abdullah and Gerhauser, 2008). Char and inorganic content of bio-oil are important for its aging characteristics, as they appear to catalyze polymerization reactions during storage, leading to viscosity increase. Moreover, during storage along with viscosity increase, growth of the apparent diameter of the suspended char has been observed (Diebold, 2000).

As far as instability aging is concerned aldehydes have been identified as the most unstable fraction (Diebold, 2000). They react with alcohols to form hemiacetals, acetals and water; with water to form hydrates; with phenolics to form resins and water; with proteins to form dimers and with one another to form resins and oligomers. In addition, acids react with alcohols in esterification reactions to form esters and water as well as with mercaptans to form dimers.

Any bio-oil containing olefin will polymerize to form oligomers and polymers. As mentioned above air oxygen oxidizes the bio-oil and reactive peroxides are formed along with acids, which catalyze polymerization reactions of unsaturated products.

Those reactions change the polarity of the total mixture and increase phase separation since the total mutual solubility is decreased (Diebold, 2000).

The above-mentioned reactions can be accelerated with temperature increase. During heating four different stages have been reported (Lu *et al.*, 2009): thickening, phase separation, gummy formation (at around 140°C) and coke formation at higher temperatures. Simple methods such as addition of polar solvents, diesel or other fuels can address some of those characteristics.

8.3.2.1.7 Health and safety

Bio-oil can be characterized as inherently biodegradable. This has been verified by (Blin *et al.*, 2007) after performing a 28 days biodegradability test. Results revealed bio-oil shows a biodegradability of 41–50%, which is higher than those of diesel fuels (Piskorz and Radlein, 1999). The biodegradability of bio-oil is quite important because in case of an accident, bio-oil would be degraded even faster than fossil fuels. The large number of compounds in bio-oil raises concerns about human health and other related environmental effects. Because this is an important issue to the eventual commercialization of this technology, researchers began to investigate the health effects of bio-oil.

As mentioned above, bio-oil is comprised of more than 300 compounds and some of them such as benzene and phenanthrene are known to have carcinogenic effects. In addition, there are many compounds in bio-oil that have not been identified and thus their effects on living organisms are unknown yet.

The oils produced in the range of 500–600°C, show no mutagenic activity. However, it has been reported that when bacteria were exposed to oils produced at the highest severity a marked increase in mutagenicity noted (Ringer *et al.*, 2006). Similar studies with samples of bio-oil produced using different biomass feedstocks and different processes, showed some controversy.

Hardwood and softwood pyrolysis oil samples displayed mutagenic activity but only slightly when compared to a benzo(a)pyrene standard. However, these results were considered to be inconclusive (Ringer *et al.*, 2006). The low severity oil showed no carcinogenic effects, however, exposure to the higher severity oils definitely showed a positive carcinogenic response. The result is consistent with the experience seen in the coal tar industry where exposure to polycyclic aromatic hydrocarbons (PAH) was correlated with high incidence of cancer (Ringer *et al.*, 2006).

8.3.2.1.8 Other important properties

Other important properties when considering bio-oil as fuel for heat and power applications are the flash, pour and cloud points, which indicate the easiness of ignition, lowest flow temperature and crystalloid structure of waxes respectively. All of them are important in combustion processes. Typical values as well as test method for those properties are shown in Tables 8.3 and 8.5, respectively.

Due to differences in properties and nature comparing to diesel fuel, special or slightly modified analytical techniques should be applied for determination of its properties. The main properties and the corresponding analytical methods are listed in Table 8.5.

8.3.2.2 Bio-oil applications

The ecological advantages from biomass utilization in conjunction with oil prices and reserves and the political instability that characterizes many of the oil-producing countries have made biomass an integral part of primary energy sources. Biomass is CO₂-neutral with low sulfur content and thus a liquid product deriving from biomass would exhibit the same benefits. The production of bio-oil converts raw biomass into a liquid with energy density 6 to 7 times higher than wood. The increase in energy density increases the amount of energy that can be transported by conventional means (tanker trucks) (Badger and Fransham, 2006). De-coupling of bulky solid fuel handling from the processing facility is advantageous since it will reduce the capital investment and operation costs and furthermore, liquids are easier to be handled (Chiaramonti *et al.*, 2007).

Table 8.5. Analytical methods for bio-oil characterization (Oasmaa and Peacocke, 2010).⁵

Analysis	Method	Sample size
Water [wt%]	ASTM E 203	1 g
Solids [wt%]	ASTM D7579	30 g
Particle size distribution	Optical methods	1 g
Carbon residue [wt%]	ASTM D 189	2–4 g
Ash [wt%]	EN 7	40 mL
CHN [wt%]	ASTM D 5291	1 mL
S & Cl [wt%]	Ion chromatography	2–10 mL
Alkali metals [wt%]	Atomic Absorption Spectrometry (AAS)	50 mL
Metals [wt%]	Inductively Coupled Plasma (ICP), AAS	50 mL
Density (at 15°C) [kg/L]	ASTM D 4052	4 mL
Viscosity (at 20, 40°C) [cSt]	ASTM D 445	80 mL
Viscosity [mPa s]		40 mL
Pour point [°C]		80 mL
Heating value [MJ/kg]	DIN 51900	1 mL
Flash point [°C]	ASTM D 93	150 mL
Acidity	pH meter	50 mL
Total Acid Number	ASTM D 664	
Water insolubles [wt%]	Water addition	5 mL
Stability	80°C, 24 hours	200 mL

8.3.2.2.1 Heat and power

Existing oil-fired burners cannot be fuelled directly with solid biomass without major modifications and/or reconstruction. This is not economically attractive, and moreover liquid products are easier to handle and transport. Existing combustion applications require only relatively minor or even no modifications of the existing equipment in order to run on bio-oil. Bio-oil is a more attractive alternative fuel for power applications than black liquor and it is economically feasible to use bio-oil to substitute for fuel oil in burners and boilers to produce heat and power.

Red Arrow Products used a swirl burner to combust different mixtures of pyrolysis by-products to produce heat (Freel *et al.*, 1996). Neste Oy tested the operation of a dual burner on bio-oil without auxiliary fuel and only minor modifications needed to improve the combustion stability; while CO and NO_x emissions were at acceptable levels, but particulate emissions were two times higher than fuel oil (Gust, 1997). Similar results have been reported by (Oasmaa *et al.*, 2001) using several bio-oil samples in an 8 MW_t furnace.

A successful integrated pilot plant employing a fluidized bed pyrolysis of biomass for bio-oil production and subsequent use of the bio-oil in fluidized bed boiler has been demonstrated by a consortium of Metso, Fortum, UPM and VTT to provide district heating (Lehto *et al.*, 2010; PyNe, 2011). Boilers and furnaces are mostly used to produce heat and the potential of using bio-oil has been realized (District Energy, 2007). However, bio-oil can be used in co-firing applications for power generation. Generally, in coal-fired power stations, bio-oil and char can be co-combusted, which corresponds to 85% biomass-to-fuel energy efficiency. Bio-oil has been tested in natural gas fired power stations and results showed that can be co-fired resulting in a 70% biomass-to-fuel energy efficiency (Wagenaar *et al.*, 2012). The deposits of the bio-oil combustion on the oil guns have been reported to be comparable to fuel oil combustion (Wagenaar *et al.*, 2012).

Generally, in order to use pure bio-oil directly in burners and boilers, preheating to 70–80°C prior to combustion is needed to reduce the viscosity without recirculation of heated product back to the storage tank. Furthermore, startup and shutdown on conventional fuel should be carried

⁵For more information the reader should consult the original references in Oasmaa and Peacocke (2010).

out, to avoid deposition and coking of nozzles (Oasmaa *et al.*, 2005). The use of bio-oil in burners has been successful at demonstration and commercial scale (Lozowski, 2009). In addition to boilers, Stirling engines have been considered for the application of bio-oil as an alternative fuel (Czernik and Bridgwater, 2004). Diesel engines offer a high efficiency (up to 45%) in power generation and can also be used in combined heat and power processes. Diesel engines offer a high power-to-heat ratio and they maintain high efficiency even on partial load. They can operate using a relatively vast fuel spectrum and even on low-grade fuels. Furthermore, their relatively low capital investment and operating costs make them an even more attractive option (Solantausta *et al.*, 1994). Solantausta *et al.* (1994) performed tests using a medium speed diesel engine running on bio-oil. They concluded that an auxiliary fuel should be used during start-up due to the poor ignition properties of bio-oil. However, once ignited, bio-oil is combusted readily. The emissions levels in terms of CO, NO_x, THC and smoke were similar to reference fuels (Solantausta *et al.*, 1994).

Similar tests from same research group on a high speed diesel engine showed that auto-ignition of bio-oil could not be achieved without additives (Solantausta, 1993), however use of bio-oil in high speed diesel engines is feasible if blended with methanol and cetane improving additives (Czernik and Bridgwater, 2004). Bio-oil combustion in diesel engines is kinetically controlled contrary to diesel fuels where mixing is the limiting step with the thermal efficiency of bio-oil being almost equal to diesel fuels (Leech, 1997). Long tests performed on slow speed diesel engine showed that bio-oil can be used solely without any problem and with lower emissions than diesel fuels (Ormrod and Webster, 2000).

Summarizing, the main concerns for operating diesel engines on bio-oil are some specific properties such as difficult ignition, corrosiveness and coking. Those problems are not as severe or serious as first thought and many organizations proceed with successful developments.

Bio-oil has also been used in power plant gas turbines. Gas turbines can be modified to accommodate some of the properties of biomass pyrolysis oils. Bio-oil use in gas turbines has been investigated since the 1980s. In those initial tests, the measured combustion efficiency was 95%; however, it projected that it could exceed 99% under optimum conditions.

Since then, several other tests in gas turbines have taken place with most of the reports indicating corrosion and fouling problems (Strenziok *et al.*, 2001; Moses, 1994). As mentioned above, alkali (especially of metals of potassium and sodium) in bio-oil can form low melting compounds that stick to the hot turbine blades and then and subsequently corrode these components (alkali hot corrosion). Another difference compared with diesel fuel combustion in gas turbines is the decreased range of efficient operation of the combustor. Moreover it has been reported that bio-oil, tends to generate acoustic instabilities of low frequency (Lopez Juste and Salva Monfort, 2000). Under good operating conditions of the gas turbines, the emissions with bio-oil are similar when compared to diesel or fuel oil, while the emission of acidifying SO₂ is nearly absent (Hoogendoorn *et al.*, 2007). Recently bio-oil has successfully been used in turbines in commercial scale (<2.5 MW_e) by Dynamotive Energy Systems in collaboration with Orenda Aerospace Corporation using a OGT 2500 gas turbine with coated blades to avoid corrosion from alkali metals. (Dynamotive Energy Systems, 2012). The future for bio-oil use in gas turbines is bright and will offer the shortest payback time and the lowest financial risk (Hoogendoorn *et al.*, 2007). In Tables 8.6–8.8 emissions from different tests when using bio-oils for heat and power applications are reported.

From the above-mentioned one can note that there are limitations and challenges using bio-oil for heat and power applications even though commercialization has been achieved. Market penetration, though, needs standardization and thus norms and standards for its use in different heat and power generation systems are needed. However, no global standards had been set until 2009 when bio-oil was approved and established as ASTM D 7544 standard (Oasmaa and Peacocke, 2010). Table 8.9 shows the ASTM burner fuel standard for pyrolysis liquid fuel.

There are additional benefits from using bio-oil for heat and power applications. Intermediate storage of bio-oil allows for power plants to use it in high peak consumption periods while economics of power generation suggest that a niche of up to 10 MW_e is available for exploitation

Table 8.6. Engine and burner emissions (Oasmaa *et al.*, 2005).⁶

	250 kW _e Mirrlees, 6 Cylinders, Diesels, UK		Ormrod	25 kW _e Stirling Engine, FLOX Burner, ZSW, Germany
	7%wt pilot fuel ⁷	17%wt pilot fuel ⁸	100%wt pilot fuel ⁸	no pilot fuel
Liquid source	BTG			BTG
Feedstock	Mixed hardwood			
Solids [wt%]				0.35
O ₂ [wt%]	15	15	15.8	6–10
CO [ppm]	3475	2057	271	<35–125
CO ₂ [vol%]	4.4	4.6	3.9	
NO [ppm]	240	313	510	
NO ₂ [ppm]	41	77	76	
NO _x [ppm]	384	266	586	20–95
SO _x [ppm]	0	33	86	
THC [mg/m ³]				20–40

Table 8.7. Normalized emissions of various fuels types of maximum turbine load of 2.5 MW_e (Oasmaa *et al.*, 2005).

Fuel	Emissions (%) ⁹			
	CO ₂	CO	NO _x	SO ₂
No. 2 Diesel oil	4.2	1	321	7
Biofuel ¹⁰	4–6	49–55	58–60	1–2
Crude oil Blend	4.4	14.8	326	421
Biodiesel	4.3	4.1	321	1.4
Ethanol	4.5	3	101	2
Ontario emissions limit	60	189	86	

(Bridgwater, 1999). Nevertheless, in some areas if the economic benefits (taxes on SO_x, NO_x and CO₂) from reduced emissions are not taken into consideration then power generation from bio-oil may not be economically feasible (University of New Hampshire, 2002). Additionally, use of bio-oil instead of fuel oil for heat and power applications will allow the use of middle distillates for transportation fuel production (Chiaramonti *et al.*, 2007).

8.3.2.2.2 Gasoline and diesel fuels

As discussed above, some of the properties of bio-oil affect its fuel quality negatively and slow their application and adaption to the power generation market. Accounting that the demand for liquid fuels (diesel and gasoline) will see a net rise of 75% through 2040 (Exxon Mobil, 2012), it is easily understood that there is an increased need for an upgraded better quality fuel.

Solids content creates many problems if not handled properly, while low heating value, incompatibility with conventional fuels, high viscosity, low volatility, and chemical instability are related to oxygen content.¹¹

⁶For more information the reader should refer to original references in Oasmaa *et al.* (2005).

⁷Diesel used as pilot fuel.

⁸Flameless oxidation.

⁹All gaseous emissions have normalized to 15% O₂.

¹⁰Bio-oil from Dynamotive and Ensyn.

¹¹Usually oxygen in liquid products increases the polarity, which hinders blending with present fuels.

Table 8.8. Examples of boiler emissions for various liquid sources (Oasmaa *et al.*, 2005).

	Ensyn		Union Fenosa ^a		Ensyn			Ensyn	Dynamotive	Fortum
Feedstock	Hardwood		Eucalyptus		Hardwood			Hardwood	Pine	Spruce
Solids [wt%]	0.5							−0.4	0.17	0.05
Boiler type	Arimax		Arimax		Water-wall			10 MW _t	10 MW _t	300 kW _t
	Eetta		Eetta		utility			boiler,	boiler,	LFO
	200 kW		200 kW		boiler			Oilon Lenox	Oilon Lenox	boiler
					10 MW _t			GRT-5L	GRT-5L	
O ₂ [vol%]	4	6	5	6	32	32	67	3.3–3.6	3.3–3.4	3–4
CO [ppm]	32	28	40	20	195	198	208	1–2	10–25	10–20
NO _x [ppm]	142	137	170	150	0.8	1	1.4	159–164	108	100–150
THC					105	144	161			
Particulate matter [mg/MJ]								15	92	
Bacharah No.	5	5	2.5	2.8				2	2.8	1–2 ^b

^aWith an additional 3 wt% of ethanol and 3 wt% of water, modified refractory in boiler to ensure complete combustion, bubbling fluidized bed (BFB).

^bParticulate emissions contain only inorganic materials. No tars found. Amount is dependent on the ash content of the oil.

Table 8.9. ASTM burner fuel standard D7544 for pyrolysis liquids (Oasmaa and Peacocke, 2010; Reno, 2009).

Property	Specification	Units	Test method
Gross heat of combustion	15 min	[MJ/kg]	ASTM D240
Water content	30 max	[mass%]	ASTM E203
Pyrolysis solid content	2.5 max	[mass%]	ASTM D7544 Annex I
Kinematic viscosity at 20°C	125 max	[mm ² /s]	ASTM D445
Density at 20°C	1.1–1.3	[kg/dm ³]	ASTM D4052
Sulfur content	0.05 max	[mass%]	ASTM D4294
Ash content	0.25 max	[mass%]	ASTM D482
pH	Report		ASTM E70-07
Flash point	45 min	[°C]	ASTM D93 Procedure B
Pour point	−9 max	[°C]	ASTM D97

Thus the major challenge with all biomass conversion strategies is to remove in an efficient manner the oxygen from the hydrophilic biomass-derived feedstock and convert it into a hydrophobic molecule with the appropriate combustion or chemical properties.¹² Some of those deficiencies can be improved using physical methods while others require more complex chemical processing for complete restructure of the molecules.

The simplest way to use bio-oil as a transport fuel seems to be a combination with diesel directly. Although the bio-oil is immiscible with hydrocarbons, it can be emulsified by the aid of surfactants; however, use of surfactants may be expensive. Emulsified bio-oil is found to be more stable than the original one (Chiaromonti *et al.*, 2003). Emulsification of bio-oil with No. 2 Diesel by CANMET surfactant produces a fuel with lower viscosity than the original bio-oil while corrosiveness is about half that of bio-oil. However, even though emulsification does not demand

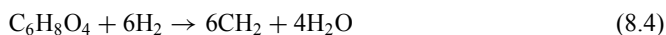
¹²Complete deoxygenation is not always necessary, as small amounts of oxygen may provide power and/or reduce soot formation.

redundant chemical transformations, the high cost of surfactants and the energy consumption for emulsification cannot be overlooked (Ikura *et al.*, 2003).

Esterification of bio-oil by addition of solvent reactions has also been proposed; however, both routes (solvent addition and emulsification) seem meaningful to prevent phase separation and enhance stability (Ioannidou and Zabaniotou, 2007). Another route for bio-oil upgrading is the reaction with olefins in the presence of catalyst to produce less hydrophilic oxygenated compounds (Zhang, Z. *et al.*, 2011). Several other routes for production of liquids in the range of diesel and gasoline pools have been suggested. Most of them are based on already developed methods for hydrocarbon fuels, since the existing infrastructure in the oil refining industry could possibly be utilized with little or no significant modification for production of fuels and/or chemicals.

8.3.2.2.1 Hydrodeoxygenation

The most investigated alternative for production of transportation fuels from bio-oil is hydro-treating and hydrocracking of the raw oil. This treatment enhances the hydrodeoxygenation (HDO) of the oil producing high quality fuel. HDO is closely related to the hydrosulfurization (HDS) used in the oil refining industry, for sulfur elimination from organic compounds (Corma and Huber, 2007). HDO use hydrogen under high pressure in the presence of catalyst to remove oxygen and the final product can be described as naphtha equivalent (CH_2) (Bridgwater, 1994). The general conceptual reaction describing the several deoxygenation reactions during the hydro-treating process can be written as follows:



The above reaction scheme suggests that the whole process is limited by the carbon content in the system and the stoichiometric yield of hydrodeoxygenated product is limited to 58.3% of bio-oil on a mass basis, without considering the H_2 requirements.

Given that bio-oil is made up of a wide range of classes of organic compounds, which behave differently under different reaction conditions, it is quite difficult to draw general conclusions from the hydro-treating process. However, there are numerous interesting insights into bio-oil hydro-processing that have been gained in recent years. HDO is normally carried out at a temperature range of 220–600°C and pressures of 35–190 bar (Mercader *et al.*, 2011; Corma and Huber, 2007). During HDO, reactions are exothermic and equilibrium calculations propose temperatures of at least 600°C to achieve full conversion.

The most frequently used catalysts in HDO of bio-oil are Co-MoS₂ and Ni-MoS₂ since they are used in traditional oil refinery hydro treating processes (Elliot, 2007; Badawi *et al.*, 2011; Samolada *et al.*, 1998; Zhang *et al.*, 2010) among others. The use of promoted Mo catalysts improves their hydrothermal stability (Badawi *et al.*, 2011). Noble metal catalysts have also been proposed for HDO process with some of them showing better results than traditional sulfide catalysts (Wildschut *et al.*, 2009); for example, it has been reported that for batch type experiments under mild HDO conditions (250°C, 100 bar for 4 h) Pt/C catalyst has 43%wt oil yield with oxygen content less than 19%wt. However in the same study it was noticed that some oils had low viscosity, whereas others were highly viscous or even semisolid (Wildschut *et al.*, 2009). Use of Pd in HDO of bio-oil has been reported to have reforming activity producing H_2 which is important for the process and is a limitation factor for this technology. For minimum hydrogen consumption during bio-oil hydro processing, HDO must be carried out with minimum or no saturation of the aromatic rings (Elliot, 2007).

For hydro treated bio-oil, TAN measurement can be used to address changes in acidity and also stability because of the relationship of the bio-oil oxygen content with TAN (Oasmaa, 2010).

Results of hydrodeoxygenated bio oil are reported in Tables 8.10–8.12.

The feasibility of hydro processing bio-oil for transportation fuels has been assessed by few studies (Wright *et al.*, 2010; Jones *et al.*, 2009). Even though hydro processing is economically attractive the key factor for fuel cost is the availability of hydrogen, especially in remote areas, while in centralized processing units the cost of transporting biomass feedstock is a limiting factor in the size of a biomass processing plant. Therefore, the production of motor fuels from biomass

Table 8.10. Low temperature catalytic hydro treating of Ensyn bio-oil (Elliot, 2007).

	Bio-oil	Upgraded bio-oil
C [wt%]	52.9	not reported
H [wt%]	6.2	not reported
N [wt%]	0.2	not reported
O [wt%] (by difference)	40.7	not reported
Acetone insoluble [wt%]	2.98	not determined
Ash [wt%]	0.2	0
TAN	100	5
pH	3.17	6.5
Moisture content [wt%]	24.8	34.3
Density [g/mL] at 20°C	1.21	0.98
Viscosity [CPs] at 20°C	179	not determined
HHV [MJ/kg m.f.]	19.4	not reported
n-pentane solubles [wt%]	0.25	47.89
Asphaltenes (benzene soluble) [wt%]	4.27	35.6
Residue [wt%]	95.48	16.51

Table 8.11. Low temperature catalytic hydrotreating of Union Fenosa bio-oil (Elliot, 2007).

	Bio-oil feedstock	Upgraded bio-oil
Hours on stream	7.5	12
Liquid hourly space velocity		
LHSV [vol oil/(vol cat h)]	0.51	0.55
H ₂ feed vol/vol	2228	2048
Bed temperatures [°C]		
Bed entrance	114	116
Bed middle	254	255
Bed exit	273	275
Liquid products [g/h]	45.7	58.2
H ₂ consumption [L/kg]	207	
Liquid recovery [wt%]	80.2	93.9
Deoxygenation [%]	45	
	Elemental analysis	
C [wt%]	51.5	62.2
H [wt%]	6.2	7.5
N [wt%]	0.5	0.5
O [wt%] (by difference)	41.7	29.8
Acetone soluble [wt%]	2.62	0.31
Ash [wt%]	0.11	0.03
TAN	85.6	5
pH	3.43	6.5
Moisture content [wt%]	16.7	3
Density [g/mL] at 20°C	1.27	1.07
Viscosity [cPs] at 20°C	1150	not reported
HHV [MJ/kg, m.f.]	19.3	26.4
n-pentane solubles [wt%]	not reported	21.1 (65.2C, 7.7H, 0.3N, 26.8O)
Asphaltenes (benzene soluble) [wt%]	not reported	30.4 (66.7C, 7.8H, 0.4N, 29.8O)
Residue [wt%]	not reported	48.5 (58.2C, 6.3H, 0.5N, 34O)

Table 8.12. Properties of fast pyrolysis oil and hydrotreated product (Elliot, 2007).

	Bio-oil	Hydrotreated product
Density [g/mL]	1.12	0.93
C [wt%]	60.4	87.7
H [wt%]	6.9	8.9
O [wt%]	41.8	3
N [wt%]	0.9	0.4
HHV [MJ/kg]	21.3	41.4
Solubility in methanol [wt%]	99	
Solubility in toluene [wt%]	Little	100

through pyrolysis and hydro processing becomes more favorable if the facility can be closely associated with an existing petroleum refinery to leverage its infrastructure (Jones *et al.*, 2009). However, those studies suggest that bio-oil upgrading process requires further development to reduce uncertainties in costs (Wright *et al.*, 2010; Hsu, 2011). Techno-economic study of PNNL points out that the biggest impacts of technical improvements are in the area of catalysis as far as bio-oil upgrading is concerned while pyrolytic catalytic processing that leads to a better quality bio-oil requiring less upgrading would also reduce product costs (Jones *et al.*, 2009).

There is significant research activity in hydro treatment of bio-oil and the reader should refer to other sources such as Mortensen *et al.* (2011). One of the latest achievements in hydro processing is concepts like the IH2 process by GTI which an integrated hydro pyrolysis and hydro conversion process (Marker *et al.*, 2009). Integrated upgrading approaches as hydro processing followed by fluid catalytic cracking appears to possess synergistic benefits. The production of commodity chemicals via hydro processing and catalytic cracking routes within the bio refinery infrastructure may enhance the economic viability of pyrolysis and pyrolysis-related processes (Butler *et al.*, 2011).

8.3.2.2.2.2 Catalytic cracking and upgrading of bio-oil

Bio-oil upgrading can also be achieved by catalytic cracking. The upgraded bio-oil is more viscous and has a higher aromatic content. Several kinds of catalysts have been used for catalytic upgrade of bio-oil. Catalytic upgrading of bio-oil can take place online or after non-catalytic pyrolysis of biomass. However, a combined process has the superiority of increasing the liquid yield and improving the product quality over two separated processes (Li *et al.*, 2008). The *in-situ* catalytic upgrading of pyrolysis vapors will be discussed in next section.

ZnO is reported to be a mild catalyst on the composition and stability of bio-oils in the conversion of pyrolysis vapors, and the liquid yields were not found to be substantially reduced. After heating at 80°C for 24 h, the increase in viscosity was significantly lowered for the ZnO treated oil (55% increase in viscosity) compared to the reference oil without any catalyst (129% increase in viscosity) (Nokkosmaki, *et al.*, 2000). Despite the indicated deactivation of the catalyst, the improvement in the stability of the ZnO treated oil was clearly observed.

Pd deposited on carbon nanotubes and MgO has been used as a biphasic catalyst between water and oil phases. During this treatment hydrodeoxygenation is achieved with parallel condensation of hydrophilic molecules (Crossley *et al.*, 2010).

8.3.2.2.2.3 Gasification, H₂ and Fischer Tropsch fuels

Another way to upgrade fast pyrolysis products is the gasification for production of synthesis gas with the latter being used for production of Fischer Tropsch (FT) fuels or alcohols.

Produced oil can be mixed with char to produce bio-slurry, which can easily be fed to gasifiers, even in pressurized applications, for more efficient exploitation. Even though a part of the energy content of the raw biomass is lost in the pyrolysis process, ease of use of the bio-slurries and

Table 8.13. Comparison between bio-oil and solid biomass gasification. Adapted from Bridgwater (2012).

Impact of using liquid bio-oil	Capital cost	Performance	Product cost
Transport costs	Lower	Higher	Lower
Very low alkali metals	Lower	Higher	Lower
Handling and transporting costs	Lower	None	Lower
Liquid feeding to gasifier particularly pressurized	Lower	Higher	Lower
Lower gas cleaning requirements	Lower	Higher	Lower
Higher cost for fast pyrolysis	Higher	Lower	Higher
Lower efficiency from additional processing step	Lower	Higher	Higher

improved economies make up for this loss (Bridgwater, 2012). The effects on overall economy and efficiency from the synergy of biomass pyrolysis and gasification are shown in Table 8.13.

Apart from synthetic hydrocarbon fuels, which can be blended directly with conventional ones, H_2 can also be produced from steam reforming of bio-oil using a similar approach as conventional methane reforming over Ni based catalysts (Kechagiopoulos *et al.*, 2009 among others).

It can be understood that the advantageous properties of bio-oil make fast pyrolysis of biomass an integral part of a biorefinery. Biorefineries based on biomass pyrolysis will be able to access a wider variety of feedstock from different areas. Several commercial and demonstration plants around the world are built (or scheduled to be built) that have biomass pyrolysis as the core process for liquid fuels production (Lozowski, 2011).

8.4 MODELING

The upsurge of interest in the design and optimization of the pyrolysis reactors requires process descriptive models. Thus, knowledge of the kinetics governing the thermal decomposition of the lignocellulosic materials is required. Given, that biomass pyrolysis involves numerous and complex reactions, which end up with the large number of products mentioned above, an exact reaction mechanism and kinetic modeling for biomass pyrolysis is extremely difficult, hence pyrolysis typically is described by lumped models containing conceptual or pseudo-reactions. Researchers have proposed different reaction schemes through the years but even today it is difficult to develop a precise kinetic model taking into account all the parameters. The proposed mechanisms can be classified into three broad categories (Peters and Bruch, 2003). Those include (i) one step models; (ii) models with competing reactions and (iii) models with secondary reactions.

8.4.1 One step models

One step models consider a simple reaction scheme where biomass decomposes following an Arrhenius type first order reaction to produce volatiles and coke with a fixed amount of char. The predicted total yields and the product ratios are based on experimental results. Those kinds of models do not represent the real situation and are oversimplified. The overall kinetic scheme is shown in Figure 8.9.

8.4.2 Models with competing parallel reactions

The classical model for wood pyrolysis is based on a competitive parallel reaction assumption. It was developed by Thurner and Man (1981) and it features a varying char yield. In this model secondary reactions are lumped with primary reactions by means of three competitive reactions (Fig. 8.10).

Another model based on competitive reactions has been proposed by Grønli. This model is based on four wood constituents (Prakash and Karunanithi, 2008). This scheme considers a fixed

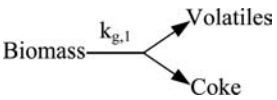


Figure 8.9. One step reaction model for biomass pyrolysis. Adapted from Peters and Bruch (2003).

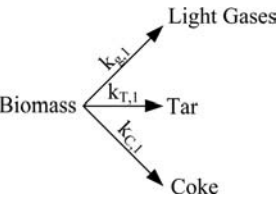


Figure 8.10. Competitive reactions pyrolysis model. Adapted from Prakash and Karunanithi (2008).

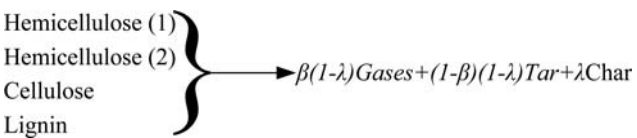


Figure 8.11. Complete reactions pyrolysis model based on different wood constituents. Adapted from Prakash and Karunanithi (2008).

char yield and doesn't include any secondary reactions. Grønli's proposed reaction scheme is shown in Figure 8.11.

8.4.2.1 Models with secondary reactions

The most comprehensive reaction schemes include the secondary reactions. One of the first models was developed by Broido *et al.* (1975) while studying the cellulose pyrolysis. In his study it was shown that cellulose decomposes by a multistep mechanism at low temperatures. Bradbury *et al.* (1979), have modified Broido's reaction scheme and its kinetic parameters to a model known as "Broido-Shafizadeh model". This mechanism accounts for the formation of an active cellulose (also named as "anhydrocellulose") intermediate and two competing reaction pathways: (a) intermolecular dehydration and ring scission predominating at low temperatures, leading to char and gas; and (b) end-group depolymerization, leading to tar. The reactions are endothermic and their rates are represented as first order in the mass of pyrolyzable material and with an Arrhenius type of temperature dependence (Prakash and Karunanithi, 2008; Di Blasi, 1998). The latter model was extended to include secondary tar cracking (Liden *et al.*, 1988). The extended model's overview is presented in Figure 8.12. The existence of "active cellulose" intermediate proposed above, has been heavily questioned by several researchers (Koufopoulos *et al.*, 1991; Varhegyi *et al.*, 1997) and hence is usually omitted from the scheme.

Similarly to Grønli's approach based on wood constituents, Koufopoulos *et al.* (1989) correlated the overall biomass pyrolysis rate as a sum of the rates of the major biomass components. According to the mechanism there is a zero order reaction taking place at low temperatures and it is not associated with any mass loss from the solid biomass. The "intermediate" product then decomposes *via* two competitive reactions to form volatiles, gases and char. The formed products take part in secondary reactions described by first order kinetics.

The Koufopoulos kinetic scheme (Fig. 8.13) has been used in numerous of simulations because of its capability to predict the final char yield. However, the weak point is the inability to determine

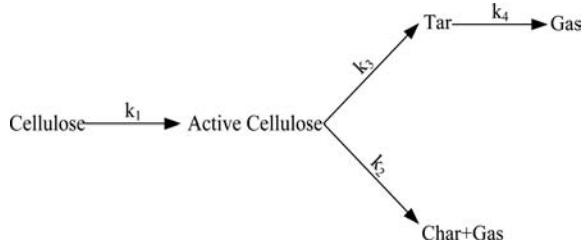


Figure 8.12. Modified Broido-Shafizadeh model.

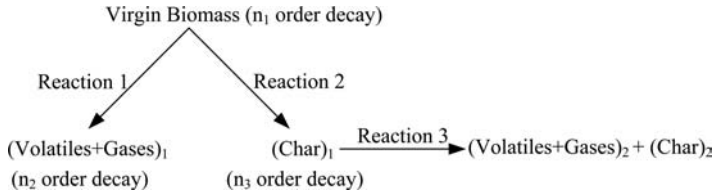


Figure 8.13. The Koufopoulos kinetic scheme.

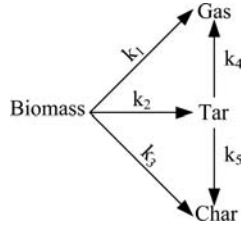


Figure 8.14. Mechanism of wood pyrolysis proposed by Shafizadeh and Chin. Adapted from Shafizadeh and Chin (1977).

liquid yield since no distinction between volatiles and gases is made. A model based on Shafizadeh and Chin's suggestion (Shafizadeh and Chin, 1977) of wood decomposition, where produced tar further reacts to produce gases and char, seems more appropriate to determine the liquid yield.

The primary reactions 1–3 can be described by equation (8.5) (Di Blasi, 1993):

$$r_i = k_{0,i} e^{-(E_i/RT)} (1 - \varepsilon) \rho_w, \quad i = 1, 2, 3 \quad (8.5)$$

where $k_{0,i}$ [1/s] and E_i [J/mol] are the pre-exponential factor and the activation energy of the i th ($i = 1, 2, 3$) reaction respectively; R [J/molK] is the universal gas constant, T [K] is the temperature, ε [–] is the porosity (both micro and macro) of the particle and ρ_w [kg/m³] is the density of wood.

Secondary reactions 4 and 5 are tar concentration dependent and can be described by equation (8.6):

$$r_i = k_{0,i} e^{-(E_i/RT)} \frac{y_T P}{RT} M_T, \quad i = 4, 5 \quad (8.6)$$

where $k_{0,i}$, E_i , R , T represent the same quantities as in equation (8.5) and refer to reactions 4 and 5 (Fig. 8.14). P is the pressure, y_T is the tar fraction and M_T is the molecular weight of tar.

The literature teems with published values of kinetic parameters; however, here it should be emphasized that determination of kinetic parameters requires a careful experimental design and

Table 8.14. Kinetic parameters of biomass pyrolysis model with secondary cracking.

Reaction ¹³	k_0	E_i	Reference
1	$1.11 \times 10^{11} \text{ [s}^{-1}\text{]}$	$177 \text{ [kJ mol}^{-1}\text{]}$	Wagenaar <i>et al.</i> (1993)
2	$9.28 \times 10^9 \text{ [s}^{-1}\text{]}$	$149 \text{ [kJ mol}^{-1}\text{]}$	Wagenaar <i>et al.</i> (1993)
3	$3.05 \times 10^7 \text{ [s}^{-1}\text{]}$	$125 \text{ [kJ mol}^{-1}\text{]}$	Wagenaar <i>et al.</i> (1993)
4	$8.6 \times 10^4 \text{ [s}^{-1}\text{]}$	$87.8 \text{ [kJ mol}^{-1}\text{]}$	Liden <i>et al.</i> (1988)
5	$7.7 \times 10^4 \text{ [s}^{-1}\text{]}$	$87.6 \text{ [kJ mol}^{-1}\text{]}$	Liden <i>et al.</i> (1991)

control in order for the pyrolysis process to be kinetically controlled and avoid heat transfer related problems (limitations due to particle size and/or amount of mass of the material, thermal lag because of very high heating rates, heat effects due to reactions etc.) that may affect the result. The experimental conditions of published data are sometimes obscure and their reliability uncertain. Published literature data that refer to a pyrolysis model with secondary cracking are shown in Table 8.14.

To avoid selection or generation of misleading experimental data a dimensionless number named the “pyrolysis number” (Py) have been introduced (Pyle and Zaror, 1984). This number is the ratio between the characteristic time for pyrolysis reaction and temperature propagation inside the particle; Py shows the relative velocity of the reaction and temperature waves. Equations (8.7) and (8.8) show the expressions for the characteristic time for temperature and reaction, respectively:

$$\tau_T = \frac{\rho C_p R^2}{K} \quad (8.7)$$

$$\tau_R = \frac{1}{k} \quad (8.8)$$

where ρ , C_p , R , K are the density, specific heat capacity, radius (or other characteristic length) and thermal conductivity of the solid particle respectively is the kinetic constant of the pyrolysis reaction.

Thus, according to the above definition the pyrolysis number is:

$$Py = \frac{\tau_R}{\tau_T} = \frac{K}{k\rho C_p R^2} \quad (8.9)$$

Large Py values ($Py \gg 1$) indicate that the heat transfer within the particle is very fast as compared with the reaction. Very small Py values ($Py \ll 1$) indicate that the reaction proceeds very fast (almost instantaneously) as compared with heat transfer inside the particle. The relative importance of internal temperature gradients is measured by the Biot number (Bi) which is defined as:

$$Bi = \frac{hR}{K} \quad (8.10)$$

where h is the heat transfer coefficient.

For large Bi , internal heat transfer is slower than the external, and temperature gradients within the particle will be significant. On the other hand, for small values of the Biot number, internal heat transfer is rapid and the temperature of the particle can be assumed to be uniform with the transfer rate determined by the value of the heat transfer coefficient. Under those conditions the relative rates of heat transfer to the particle and the intrinsic kinetics is important because internal heat transfer does not limit the process. Thus a second pyrolysis number has been introduced,

¹³Reaction numbers refer to Figure 8.14.

which is defined by the product $Bi \cdot Py$ (Pyle and Zaror, 1984)

$$Py' = Bi \times Py = \frac{h}{k\rho C_p R} \quad (8.11)$$

Kinetic control holds for $Bi \ll 1$ and $Py' \gg 1$. Thus Py , Py' , and Bi numbers are a useful tool to determine whether the value of the kinetic parameters that has been estimated from experiment or reported in literature represent intrinsic kinetics.

It should be noted that the high chemical complexity of both the biomass and the related pyrolysis products motivate the introduction of kinetic models based on kinetic laws different from those presented above. Those include free radical mechanisms as well as distributed activation energy models (e.g. Varhegyi *et al.*, 2010).

8.5 RECENT TRENDS AND DEVELOPMENTS

Bio-oil upgrading technology at centralized facilities might include gasification and synthesis, fluid catalytic cracking, hydro processing, steam reforming, etc. (Butler *et al.*, 2011). However, one of the most promising methods to improve the quality of bio-oil (minimization of undesirable properties and increase of added-value chemical compounds) is the *in-situ* heterogeneous catalysis in biomass pyrolysis.

Biomass processing with the use of catalysts has recently received additional impetus in an economic competitive environment (Murzin and Simakova, 2011), since *in-situ* catalytic pyrolysis has the advantage of being de-coupled from an integrated bio or conventional refinery which implies that it can be used in remote areas in close vicinity to the original biomass feedstock which offers the potential for optimization, greater economies of scale and further exploitation of bio refineries (Bridgwater, 2008). Furthermore, *in-situ* catalytic pyrolysis does not require re-evaporation of the condensed liquid, which would create problems due to the unstable nature of raw bio-oil as well as added costs (Samolda *et al.*, 2000). Catalytic cracking of biomass has been reported to produce 10 wt% more liquid product in comparison with the use of bio-oil as a feedstock (Park *et al.*, 2007).

In the *in-situ* catalytic pyrolysis, the catalyst is also the heat carrier, unless other means of external heating are used. Heterogeneous catalysis has been used for many years in conventional oil refineries to convert heavy hydrocarbons into suitable, fuels and chemicals. Thus using biomass catalytic pyrolysis an improved bio-oil is aimed to be suitable for use within refinery infrastructure since petroleum refineries are already built, and use of this existing infrastructure for the production of biofuels requires little capital investment (Marker *et al.*, 2005).

The improved-quality bio-oil can be processed with conventionally formed hydrocarbon fractions and further refined by FCC and/or HT processes (Stöcker, 2008).

Different kinds of catalysts have been used; those include metal oxides, zeolites, transition metal based catalysts, etc.

Metal oxide catalysts as activated alumina has reported to reduce the oxygen content of the yielded oil while at the same time decrease in bio-oil yield (Demiral and Sensöz, 2008). While other studies using the same catalyst report that activated alumina influences bio-oil yield without altering bio-oil composition (Yorgun and Simsek, 2008).

Zeolite catalysts have been shown to be more effective in the selective deoxygenation of pyrolytic vapors, resulting in the formation of decreased O/C bio-oil (Carlson *et al.*, 2008). Several zeolite structures have been tested in catalytic biomass pyrolysis such as Y, HZSM-5, Al-MCM-41, Beta, and SBA-15. Generally, zeolites with stronger acidity promote lignin fraction decomposition.

Stefanidis *et al.* (2011) have tested 15 different catalysts for online upgrade of pyrolysis vapors in fixed bed reactor and they report that the most interesting materials are zirconia/titania and a ZSM-5 formulation, which yielded organic liquid products with reduced oxygen and higher aromatics content. They also point out that the worst performance was observed using an FCC catalyst.

Table 8.15. Elemental composition of bio-oil obtained after steam pyrolysis for various feedstocks.

Temperature	Cottonseed cake 550°C		Rice straw 550°C		Bamboo 524°C	
	Static pyrolysis	Steam pyrolysis	Static	Sweeping gas	Steam	Steam
C [wt%]	65.9	73.98	65.45	65.68	70.56	74.44
H [wt%]	8.5	9.65	7.67	7.66	8.52	9.55
N [wt%]	5.7	3.05	1.18	1.08	1.03	
O [wt%]	19.9	13.32	25.7	25.58	19.89	16.01
H/C	1.55	1.56	1.41	1.4	1.44	
O/C	0.19	0.13				
Calorific value [MJ/kg]			28.53	28.61	32.58	33.54
Reference	Özbay (2001)		Pütün <i>et al.</i> (2004)		Kantarelis <i>et al.</i> (2010)	

ZSM-5 cracking and deoxygenation activity among other zeolites has been reported elsewhere and it has been reported to be the most suited for biomass catalytic pyrolysis (Mihalcik *et al.*, 2011). The use of pyrolysis gas as a fluidizing medium increases bio-oil yields (Butler *et al.*, 2011).

In conjunction with *in-situ* catalytic pyrolysis the effect of different atmospheres during pyrolysis has been studied and gains considerable attention from scientific community since the use of a gas able to modify *in-situ* the pyrolytic products seems favorable (Heo *et al.*, 2010). The effect of the fluidizing gas has been reported to influence both yield and composition. Under CO and CO₂ atmospheres the acid and ketones content of the bio-oil increases while the methoxy-containing compounds (which are regarded as polymerization precursors (Zhang *et al.*, 2009) are reduced in favor of mono-functional phenols which results in bio-oil with significantly increased HHV (as compared with N₂ atmosphere) (Zhang *et al.*, 2011).

Biomass pyrolysis in the presence of steam also favors the liquid production at the expense of char (mainly). Moreover, the solid product exhibits high surface area and well-developed porous structure, which suitable for activated carbon applications (Minkova *et al.*, 2001). Similar effects have been noted during lignite pyrolysis in a steam atmosphere. The result is equally applicable to other samples such as bituminous coal and oil shale (Minkova *et al.*, 1991). Minikova *et al.* (2001) reported that for all the biomass investigated, the total yield of liquid product obtained in steam pyrolysis is 2–4 times higher than that in nitrogen atmosphere. Experimental studies using fixed bed reactors on different biomass feedstocks showed higher calorific value of the liquid product than in N₂ atmosphere (Pütün *et al.*, 2002; Özbay *et al.*, 2001).

The effect of steam on the bio-oil yield can be attributed to the fact that steam inhibits the secondary cracking reactions of the products of pyrolysis.

The oil obtained is reported to be more paraffinic than the one obtained by static retorting (Özbay *et al.*, 2001). Table 8.15 lists elemental compositions of liquids obtained during steam pyrolysis of different biomass species. Most probably steam influences the donor-acceptor interaction and facilitates the desorption of the hydrophobically retained low molecular products from the cavities of the cross-linked molecules, and it does not act only as a carrier gas (Minkova *et al.*, 1991).

Catalytic steam pyrolysis has also been studied. The studies showed that bio-oil yield is higher under steam atmosphere while the composition of the obtained oil varies depending on the catalyst chosen. Thus, catalyst choice and reaction conditions should be further examined (Pütün *et al.*, 2008). Results from catalytic steam pyrolysis using different catalysts are shown in Table 8.16. A similar concept using heterogeneous catalysis in the presence of near critical hot water is under investigation. It is a combination of the BTO Pytec and CLC processes (Armbruster, 2011).

Table 8.16. Bio-oil composition from catalytic pyrolysis in steam atmosphere for various feedstocks.

Feedstock	Cottonseed cake	Cottonseed cake	<i>Euphorbia rigida</i>	<i>Euphorbia rigida</i>
Temperature	550°C	550°C	500°C	500°C
Catalyst	Natural zeolite (20% wt)	Natural zeolite (20% wt)	Activated alumina (10% wt)	Activated alumina (10% wt)
Atmosphere	N ₂	Steam	N ₂	Steam
C [wt%]	68.88	73.31	77.21	72.93
H [wt%]	8.73	10.09	9.68	9.81
N [wt%]	7.06	4.73	1.91	1.14
O [wt%]	14.33	11.87	11.20	16.12
H/C	1.52	1.65	1.50	1.61
O/C	0.16	0.12	0.11	0.17
Reference	Pütün <i>et al.</i> (2006)	Pütün <i>et al.</i> (2006)	Pütün <i>et al.</i> (2008)	Pütün <i>et al.</i> (2008)

8.6 CONCLUSIONS

Biomass fast pyrolysis offers additional advantages in relation to the production of second generation transportation fuels and bio-chemicals. The mobile liquid product has already been successfully used in commercial scale for heat and power applications with no adverse changes in the operation or the emission levels; nevertheless, a few problems associated with bio-oil composition need to be addressed. The main research and development efforts are now related to production of transportation fuels with a focus on catalytic pyrolysis, bio-oil upgrading processes and ASTM standards development. The main challenge is to improve the quality of the bio-oil for fuel and chemicals production since this integrated production is the most likely scenario for economic optimization. While the main challenge in the concept of bio refinery is the development of catalytic processes that can produce a high quality product, providing upgraded bio-oil from remote areas will reduce overall cost and improve the flexibility of the whole refinery. The bio-oil upgrade can take place in a centralized bio refinery or close to the biomass source. Processing of biomass in a centralized facility still seems economically unattractive and moreover other aspects such as biomass availability have to be considered.

Such a prospect can be realized using relatively inexpensive and compact fast pyrolysis-upgrading facilities. Catalytic pyrolysis for *in-situ* production of upgraded bio-oil combined with use of other agents (steam/H₂/CO₂ etc.) that seems to alter the product quality sounds promising. However, a lot of effort needs to be put in to achieve those goals.

Concluding, the heat and power generation sector has already benefitted from biomass conversion through pyrolysis and generated bio-oil, and several commercial units are operating and planned. The motor fuel and chemical sectors are yet to achieve full benefits from bio-oil, but promising developments in both processing and upgrading seem likely to achieve the goal in the short term.

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CHAPTER 9

Solid-state ethanol production from biomass

Shi-Zhong Li

9.1 INTRODUCTION

Fermentation by microorganisms can be divided into two parts: liquid-state fermentation (LSF) and solid-state fermentation (SSF) (Pandey *et al.*, 2000). SSF means that microorganisms grow on a solid medium with little or no free water, which is quite close to a natural state. SSF involves microorganism's growth and utilization of insoluble medium. Compared to LSF, SSF has many advantages: (i) SSF does not need strictly anaerobic conditions; (ii) facilities and energy costs are much lower; (iii) the product yield is higher; and (iv) the after-processing is simpler and produces only little wastewater during the process (Singhania *et al.*, 2009). Therefore, SSF has attracted a great deal of attention recently and has begun being used worldwide. However, due to the low water activity, less cell-growth uniformity, and the transfer of nutrient substance and products during fermentation, it is quite difficult to measure and control the parameters. These factors make industrialization of SSF difficult in large scale (Durand, 2003). The industrialization of penicillin in 1945 created the new era of modern industrial fermentation but also caused a trend away from SSF (Pandey, 2003). However, the production rate of some modern biological products, such as enzymes (Graminha *et al.*, 2009) and organic acids (Vandenberghe *et al.*, 2000), created through SSF is much higher than that of LSF. On the other hand, the production of wastewater, the high consumption of ventilation, and mechanical agitation have obstructed the development of LSF. Thus, researchers have done intensive research on very high gravity (VHG) fermentation (Soccol and Vandenberghe, 2003). However, the utmost form of VHG fermentation is SSF. Hence, with the recent advances in bioengineering, scientists should pay much more attention on SSF.

9.1.1 *The history of SSF*

It has been reported that as early as 3000 BC, fermentation technology by yeast was in use in the East to produce foods such as bread, alcohol, and soy sauce, etc. It is documented that the Chinese have been using microorganisms to produce different types of food since 2700 BC. The first wines were natural wines, which are made from fruits, honey, and milk through microbial fermentation. This type of wine production dates back to nomadic koumiss, approximately 8000–5000 BC (Wang, 2005). The second generation of alcohol was fermented by saccharification and a fermentation agent that is known as yeast starter (Liu and Zhang, 2010; Bao, 2005). Ancient Chinese populations used SSF quite early, dating as far back as the Longshan civilization of around 5000 BC, and wine-making became a mature industry approximately 3000 BC.

In the early 20th century, scientists first used microorganisms, predominantly fungi, to produce organic acids, enzymes, and other metabolites through the process of SSF, and introduced facilities (bioreactors) that are suitable for SSF for the first time (Sahir *et al.*, 2007). Penicillin was first discovered and produced in the 1940s, a golden period for the fermentation industry. During this period scientists mainly focused on the LSF, while the SSF was generally ignored although it was the initial method that was used for fermentation (Minjares *et al.*, 1993). The milestone developments of SSF occurred during the 1950s to '60s, during which articles about SSF using fungi were published (Kotwal *et al.*, 1998). During the 1970s, SSF was widely used for producing enriched protein (Hu and Guo, 2005) and mycotoxin (Jing *et al.*, 2009), which were used to treat cancer. Later, more attention was paid to processes using different types of media and

microorganisms on single-cell proteins, and since then, the cost of different types of fermentation has been decreasing (Martins and Mussatto, 2011).

It is difficult to understand the transfer of materials and energy that occurs when a microorganism grows on an insoluble medium, and therefore, the basic research and development of SSF technology has been slow (Hamidi-Esfahani *et al.*, 2004). With the development of modern fermentation technology, including the mathematical model and important facilities and research in kinetics, the optimization of SSF has been promoted to a high degree and has developed into a new field of biotechnology (Hashemi *et al.*, 2011). In the wake of the energy crisis and because environmental problems are becoming increasingly more serious, SSF has quickly spread to environment and protein feed (Mahanta *et al.*, 2008) production, as it is green and clean and is a low-energy consumption method. For example, people use cellulose, such as the waste products of agriculture and industry, to produce high value-added products, such as biofuel, biochemical products, biological insecticides, biological accelerants, fertilizer, and biological pulp, through SSF.

9.2 THE PRINCIPLE OF SSF

9.2.1 *Microorganisms in SSF*

SSF predominantly uses filamentous fungus and yeast. Priority choices are *Mucor* and *Rhizopus*, in the algae and bacteria; white-rot fungus, in the basidiomycete; and *Penicillium* and *Aspergillus* in the sac fungi (Mitchell *et al.*, 2004). Scientists are trying to use bacteria, such as *Staphylococcus*, to produce inulase and *Brevibacterium* to produce L-glutanic.

The key factors to consider in SSF are the strains, the type of fermentation process, and the medium and co-productions (van de Lagemaat and Pyle, 2005). The strains may not have a one-to-one relationship (Qiu, 2007). For example, *Aspergillus niger* can produce more than 21 types of enzymes, and more than 63 types of strains can produce α -amylase. There are two main aspects that should be considered: (i) the strains chosen should be suitable for the selected fermentation methods because some strains may reach their maximum capacity when using LSF; (ii) products of interest should be the only products or should account for the largest proportion of the products.

9.2.2 *The substrate in SSF*

Price and availability should be considered when choosing a substrate in the SSF process.

9.2.2.1 *The source of the substrate*

One of the advantages of SSF is that the substrate is simple, and derived predominantly from inexpensive, natural materials, and/or waste from agriculture and industry, such as cellulose, municipal waste, fossil resources, etc. The solid base in SSF not only supplies nutrients for the process, but it also affects the transfer of materials, heat, and metabolic functions as the cells' fixture (Mukherjee *et al.*, 2009).

9.2.2.2 *The character of the substrate*

The size and water content of the solid substrate are very important to a microorganism's growth and metabolic function (Nandakumar *et al.*, 1996). To make a medium easier to be used by a microorganism, it is necessary to pretreat it by alkali chemical processing and mechanical processing, such as a gas explosion, leaching, crushing, cracking or grinding. The growth of a microorganism should be attributed to the degree of valid decomposition.

9.2.2.3 *The water content of the substrate*

Controlling the water content during the process is very important, as water content is one of the key factors in a successful SSF (Ohno *et al.*, 1995). Therefore, changes of water content in the medium will affect growth and the metabolic capability of cells during SSF. The water

content inside the medium should be determined by the material's characteristics (fineness and water-binding capacity), the microorganism's characteristics (aerobic or anaerobic), and the cultivation conditions (temperature, moisture, and ventilator capacity). If the water content is too high, the substance's porosity will decrease, which may cause contamination of miscellaneous microorganisms, as it is difficult to ventilate inside the substance. However, if the water content is too low, the degree of transport of the nutrients within substrate will also be low, which will inhibit growth of the microorganism, and as the fermentation continues, the substance will be too dry for the cells to grow. The water content will also affect a substance's physical characteristics, the diffusion and utilization of nutrients, the exchange of oxygen and carbon dioxide, and the process of heat and mass transfer.

9.2.2.4 *The solid-phase properties of substance*

SSF can be divided into two types, based on the solid-phase properties (Chen and Xu, 2004; Mitchell *et al.*, 2003): (i) solid substrate SSF, using crops, such as bran and soybean cake, as well as a nutrient resource as substrate, and (ii) inert carrier adsorption SSF, using an inert solid carrier in the solid phase, and a microorganism grown on a medium attached to the solid phase. The main disadvantage in solid substrate SSF is the solid phase where the carbon source comes from. During the fermentation process, the solid phase will be degraded and will collapse, resulting in the reduction of heat and mass transfer. Inert carrier adsorption SSF can solve this problem, as it has a stable solid phase that can have positive effects on a microorganism's growth and productivity and can also make it easier to control the medium components.

9.3 THE PROCESS OF SSF

The process of SSF contains five steps: (i) pretreatment, (ii) preparation of the seed culture, (iii) cell growth, (iv) fermentation, and (v) post-treatment. The pretreatment step involves material preparation, molding, sterilizing, cooling of the materials, and feedstock. The fermentation process includes ventilation and control of the temperature, moisture, and mixing. The post-treatment consists of discharging, product extraction, etc.

9.3.1 *The characteristics of SSF*

9.3.1.1 *Cell growth and measurement of products*

Making a growth curve is one of the largest problems in SSF (Durand and Chereau, 1988; Wei *et al.*, 2006), as the growth state shows the results of parameter control during the fermentation process. The key factor to this problem is that there is little free water during fermentation, so we usually use indirect methods instead, as it is difficult to isolate cells attached to a solid phase. Currently, the developed methods of predicting the growth of bacteria are as follows: detect the components' differences (such as ATP, nucleic acids, etc.), detect changes in activities (such as enzyme activity, respiratory rate, etc.), and detect CO₂ concentration during the process (which is a simple method, but one with a low degree of accuracy).

9.3.1.2 *Sterile control*

Sterile control is required in almost all LSF, as fast growing of miscellaneous microorganisms under liquid state always makes the microorganisms of interest lose their ecological dominance. In solid state, the relatively slow growing and high ratio inoculation of the microorganism are able to ensure the SSF proceed smoothly. Therefore, an aseptic technique is not necessary for SSF.

9.3.2 *The effective factors of SSF*

There are many factors which can affect SSF such as strains, medium (substance types, pre-treatment methods, particle size, water content, and water activity), relative humidity, inoculation

quantity, fermentation temperature control, and heat control during fermentation process (Mazutti *et al.*, 2006).

9.3.2.1 Carbon and nitrogen sources

Carbon and nitrogen source types and carbon-to-nitrogen ratio are very important factors in all types of fermentation (Zhang and Wang, 2010). The carbon source can be an energy source for many microorganisms, which can be monosaccharides such as glucose, or polymers such as cellulose and starch. When determining components of the medium, cell biomass compositions should be considered. Bacteria cells mainly contain 40–50% carbon, 30–50% oxygen, 6–8% hydrogen, and 3–12% nitrogen. From the point of view of basic composition of biomass, the most important component is the carbon source, while from the point of view of dynamics, production output is dependent on the consumption of the carbon source on the basis of the yield Y_{sx} (yield of biomass/consumption of carbon source). When sugar is used as carbon source, theoretically, the value of Y_{sx} is 0.5. The nitrogen source is the second most important factor we have to calculate, based on the amount Y_{sx} and biomass composition.

9.3.2.2 Temperature and heat transfer

Temperature is important in cell growth, as it can cause changes inside cells, such as the denaturation of proteins, the inhibition of enzymes, the stimulation or suppression of specific metabolic products, and cell death. The temperature can also affect fermentation. For example, a high temperature can affect a spore's germination, growth, product formation, and spore formation, while a low temperature can affect cell growth and other biochemical reactions.

The typical effect of temperature during SSF is heat accumulation (Ashley *et al.*, 1999). This process spontaneously occurs through natural microbial growth. At the beginning of fermentation, all components of the reactor should have the same temperature, but while the process continues, the temperatures of different components change because the substance has poor thermal conductivity. However, the matrix volume contraction and reduction of pores make it much more difficult for heat transfer to occur. When the temperature rises because of heat accumulation, the activity of mesophilic microorganisms is gradually reduced, while the thermophilic microorganisms become more active. Therefore, heat transfer is the most serious problem in SSF, especially in large-scale fermentation. The metabolic heat generation rate and metabolic strength vary in different SSF systems. Compared to LSF, the problem of heat transfer makes it difficult to reach the optimum temperature, as the metabolic heat production for the unit volume of solid medium is much higher than that of liquid medium. For example, metabolic heat can yield a gradient between inside and outside temperatures of approximately 3°C/cm during the log phase (Xu and Hu, 2009).

The heat transfer process during SSF contains two aspects. One aspect is the transmission of medium heat in the granules. The other is the heat transfer between the particle surfaces during the gas phase. Most of the solid phase is organic matter that has poor thermal conductivity and no liquid phase flowing freely. Therefore, the heat transmission is quite poor during SSF. Heat transfer from the surface of the solid medium to the gas phase depends on a forced ventilation rate and predominantly depends on heat conduction, at the point of no forced ventilation. SSF also presents problems with cooling. For example, in a 20-liter rotary drum SSF reactor with 3 kg of medium, the temperature inside can reach 45°C. All of these aspects demonstrate that heat transfer is the most critical problem in SSF.

Normal heat conduction and convection method cannot meet the needs, therefore causing a temperature gradient inside solid media (Chen *et al.*, 2005). Evaporative cooling, which can emit 80% of the heat, is one of the main measures for temperature control (Khanahmadi and Roostaazad, 2006). The forced ventilation can not only provide oxygen and flush out carbon dioxide, but it can also play an important role in heat transfer and can remove metabolic heat. Evaporative cooling can be accomplished by forced ventilation and medium moisture content. Therefore, the main control method in large-scale SSF is the control of the interaction of ventilation, temperature, and moisture. Temperature is one of the key factors and should be seriously considered.

9.3.2.3 Moisture and water activity

The demand for water in solid-state fermentation is very low, so the water content in the substance and the moisture inside the reactor will greatly affect the production rate (Gervais and Molin, 2003). Water in SSF for microbial growth not only provides the environment with sufficient nutrition but also directly affects the use of oxygen for the microbes. Gas transmission is restricted by a static water film on the substrate surface layer, and microbes use this water film to grow and release metabolites. The major characteristic of SSF is the absence of free water. Thus, changes of water content in the substrate have an important impact on growth and metabolism of microorganisms. In general, the bacteria requirement for water activity is between 0.90 and 0.99; most yeast requirements for water activity is between 0.8 and 0.9; fungal yeast and a few other yeast requirements for water activity are between 0.60 and 0.70 (Ito *et al.*, 2011). During SSF, water activity will decline, due to evaporation and an increase in temperature. Meanwhile, the heat and moisture content, with ventilation control, can more effectively adjust the water activity. In SSF, controlled coupling of heat, moisture content and ventilation can effectively adjust the water activity.

9.3.2.4 Ventilation and mass transfer

Mass transfer can be divided into micro and macro processes during SSF (Chen and Xu, 2004). The micro process occurs at the cellular level. For example, cells absorb nutrients and oxygen from the environment and flush out carbon dioxide, some enzymes, other metabolites, etc. The micro process also involves diffusion of oxygen to cells, and enzymes that can degrade substrate produced by cells. Enzyme diffusion is one of the important processes inside substrate particles. As solid substrates in SSF are always insoluble, the step of degrading the solid substrate to soluble materials by cells is crucial. A continuous microporous structure of substrate can have a positive effect on enzyme diffusion, and the enzymes can enter the substrate and degrade the insoluble substrate to soluble ones. Nevertheless, the substrate can diffuse from inside the substrate, which can meet the needs of the microorganisms. However, when the amount of continuous microporous structure is quite low, enzymes can only degrade the substrate on the surface, and the microorganisms can only use the nutrition on the surface. Therefore, compared to the process during LSF, the microorganism's growth is limited by the substrate's particle gap structure.

The macro mass transfer process contains several aspects: ventilation of the bioreactor; the convection and diffusion process with the air flow under conditions without ventilation; the mass transfer between the bioreactor wall and the environment; and the shearing effect during mixing. Generally, there are five methods that can improve the mass transfer state. They are as follows: (i) using granular porous or fibrous materials as the substrate; (ii) reducing the thickness of the substrate; (iii) increasing the gaps between the substrate; (iv) fermenting with a porous shallow dish; (v) mixing the substrate or using a drum reactor.

9.3.2.5 pH value

It is difficult to detect *pH* values in SSF, as currently, there are no *pH* probes that can directly measure values from wet materials. There are two empirical methods for measuring *pH*. One method is to insert a *pH* probe inside the wet materials and squeeze the liquid to determine the *pH*. The other method is to add distilled water to the wet materials and measure the *pH* value of the water. Therefore, given the difficulty of *pH* regulation during the process, it is essential to control the initial *pH* value.

9.3.3 SSF reactors

There are approximate nine types of industrial-scale reactors: the rotary drum-type, the box-type, the disc-type, the vertical cultivation cassette-type, the tilt vaccination cassette-type, the shallow disc-type, the conveyor belt-type, the cylindrical-type, and a hybrid. These reactors can be divided into two types, based on the motion of the substrate. One type is the static SSF reactor, which includes the shallow disc- and the pillar reactor-types. The other type is the dynamic SSF reactor, which includes the mechanical mixing reactor-type and the drum reactor-type (Durand, 2003).

9.3.3.1 Static SSF reactor

Currently, SSF reactors are widely used in labs, especially the cylinder-type reactors. However, a number of reactors, such as static shallow disc-type, wooden box-type, disc-type, vertical cultivation-type, and tilt vaccination cassette-type reactors, are currently in use.

The advantages of the static SSF reactors are the following:

- This type of system is simple, inexpensive, and easy to control.
- It overcomes the disadvantage that SSF cannot use a flask to obtain enough data on the process. Therefore, it can be used as a platform that provides relatively homogenous temperature and moisture.
- It is easily autoclaved.

The disadvantages of this type of system are the following:

- This type of system cannot accurately control the moisture of the air and substrate, and can only supply the system with saturated moist air.
- It cannot provide sample analysis.
- It cannot eliminate the influence of bed enlargement during the enlarging process.

9.3.3.2 Dynamic SSF reactor

There are three types of dynamic reactors, including rotary drum, mixing, and fluidized bed. The advantages and disadvantages of each type are the following:

- Rotary drum: The advantages of this reactor include: improved transfer of heat and oxygen; a high degree of automation; microbial growth uniformity; ease in obtaining samples. The disadvantages of this reactor include: excess of mechanical components, vulnerability to pollution; potential for damage to the mycelia; ease of solid culture medium conglomeration.
- Mixing type: The advantages of this reactor include: good potential for mass transfer of oxygen and heat; ease of retaining homogeneity of the solid material; ease of diffusion of added nitrogen. The disadvantages of this reactor include: potential for damage to the mycelia; ease of solid culture medium conglomeration; existence of dead angles.
- Fluidize bed: The advantages of this reactor include: favorable potential for mass transfer of oxygen and heat; no local overheating. The disadvantages of this reactor include: high level of energy consumption for sterile air; difficult in engineering amplification.

9.3.3.3 Rotary drum SSF reactor and modeling progress

With a deeper understanding of the SSF process, and the development of modeling and calculating ability, researchers hope to use models to supply more information for the design, optimum, and control of fermentation reactors (Kargi and Curme, 1985; Han, 2001; Banerjee *et al.*, 1995; Lin *et al.*, 2006; Kalogeris *et al.*, 2003; Domínguez *et al.*, 2001; Sun and Sun, 2005; Marsh *et al.*, 2000). Presently, the amount of research of rotary drum modeling simulation is increasing. Marsh *et al.* (2000) used dyed wheat gluten particles as indicators to describe mixed conditions inside a reactor. The reactor volume is 200 L and is made of stainless steel, with a diameter of 56 cm, and a length of 80 cm. The axial diffusion coefficient is approximately 9.15 cm²/min in a drum reactor without baffle, with a rotating speed of 5 rpm.

Schutyser *et al.* (2001) put forward a two-phase model of a rotary drum reactor, including a discrete particle model (solid phase) and a continuous model (gas phase). The continuous model describes air piped out through a ventilation pipe described in the distribution of beds, while the discrete particle model describes the solid phase. Heat and mass transfer between these two phases and the growth of microorganisms are included in the two-phase model. This model is tested in a 28 L reactor. During the first 45–50 h, enough ventilation rates are used to control the temperature to the optimum value. Different scales of reactors are simulated, and the results show that this model is quite useful for reactors that require ventilation.

Schutyser *et al.* (2001) used a softball discrete particle model to simulate the mixture behavior of the solid matrix particles inside the rotary drum of a SSF reactor. In this model, the force exerted by the single particle and the subsequent particle movements can be predicted. They qualitatively and quantitatively validate the two-dimensional model through experimental process monitoring and an image analysis method. From the experiments, they found that, as the size of the packing coefficient and pick function, this model can effectively predict the mixing process. Moreover, only some of the large reactor perpendicular to the inner tube baffle can improve mixing the process. In another article, the author extended this model to a 3D model (Schutyser *et al.*, 2002), and radial and axial diffusion can be simulated. Simulations were also held for no baffle-, with baffle-, and with paddle baffle-types of fermentation reactors. In 2003, Schutyser *et al.* took heat transfer and the bed moisture distribution into consideration and corrected the model.

Hardin *et al.* (2001) conducted more studies on rotary drum reactors, and they established equations for the different parts inside reactors, based on reasonable assumptions, including the heat and mass transfer process in fermentation reactors, which were in agreement with the experimental data. However, their work mainly focuses on aerobic conditions.

A rotary drum SSF reactor is a type of hybrid SSF reactor. It can retain uniform mixing of the raw materials, while avoiding large temperature and concentration gradients, and compared to a stirring type of SSF, can reduce the damage by shearing force to the microorganisms. The methods of removing heat from SSF are one of the major factors of the industrialization of fermentation. When using a rotary drum reactor under aerobic conditions, it is easy to control the temperature and water content, such as by circling sterile air to bring out the reaction heat. However, when used under anaerobic conditions, it is difficult to control the temperature if fermentation heat is too high. However, with progress in research and theory and improvement of the effective parameters control methods, in the near future, the rotary drum SSF reactor will be applied in more fermentation systems, and it will gradually be applied on a larger scale.

In research fields addressing the theory of rotary drum SSF reactor modeling, some of the mathematical models are overly simplistic and have substantial differences with the results with actual reactors. Other mathematical models are too complicated, which increases the difficulty of calculating solutions. Because of the solid substrate, it is difficult to obtain parameters inside reactors, and it is therefore difficult to conduct theory research. In addition, the current literature on models of SSF in rotary drum reactors are predominantly based on measuring parameters transfer or experience type to establish mass transfer, heat transfer model has some reference value of other devices, but further measurement regarding the mass transfer of the heat transfer coefficient should be made in rotary drum SSF reactors. With the development of powerful computing and more experimental data, further studies should be performed on rotary drum SSF reactor models. This advanced research will result in more comprehensive models that take into consideration the influence of various complicated factors, from homogeneous trends to multiphase trends, and from one-dimensional to three-dimensional simulations. The result is the development of models more in line with actual situations.

INET in Tsinghua University, one of the first research units focused on bioenergy production, designed a process of highly efficient SSF (Li and Li, 2008) based on a combination of traditional SSF process (Wang *et al.*, 2010) and modern technology (Geng and Li, 2010). They developed a new ethanol fuel process based on an industrial scale of low-energy consumption and low pollution levels. The process is an advanced form of SSF technology, and it has successfully completed test bench experiments, pilot testing (Han and Wang, 2010), and demonstration project testing.

9.4 PROGRESS OF SSF RESEARCH

- (1) From open fermentation to close fermentation: Although it is less expensive and easier to control, open fermentation is difficult to use because of fundamental constraints, such as heat dissipation, pollution, etc.
- (2) From experience to automation controls: Not only can LSF be controlled by computers, but SSF can now also be partly controlled by computers. We can use automated controls to detect

the water content in the substrate, protein production, the concentration of dissolved oxygen, ATP and glucose, etc.

- (3) From single-microbe to microbial consortium's SSF: Certain types of microorganisms can build a small yet stable ecological environment. As it is a co-culture state, which increases the total gene capacity, a synergistic effect may exist between different strains, increasing substrate conversion and the productivity of the product of interest.
- (4) From the separate operation of upstream and downstream processes to the combination operation: Currently, most companies conduct the fermentation process and product separation process in separate steps, and they then combine these steps into a single system. However, there may be more advantages to combining these two processes into a one-step process.

9.5 APPLICATION OF SSF IN BIOMASS ENERGY FIELDS

Today, the shortage of fossil fuel resources and the worsening conditions of the environment limit modern industrial processes. Therefore, almost all countries invest heavily in new energy sources, such as solar energy, wind energy, biomass energy, and geothermal energy. Biomass energy, as the only new source of energy that can produce both energy and physical products, attracts attention all around the world. Many countries have a strategic goal of promoting biomass energy development. Since 2009, the production of bioethanol has reached 58 million tonnes, including 31.8 million tonnes from the USA (corn ethanol), 19.8 million tonnes from Brazil (sugarcane ethanol), and 1.62 million tonnes from China (predominantly corn ethanol).

Fuel ethanol is also called biofuel, fuel alcohol, and gasoline alcohol. After further dehydration and the addition of a moderate degeneration agent (gasoline), ethanol can be changed to degeneration fuel ethanol, which can be used to make a new type of blended fuel (GASOHOL), simply by mixing it with gasoline. Presently, GASOHOL, with an ethanol content of approximately 25%, can be used in vehicles without any modification, with little changes in power, and automobile exhaust pollution could be significantly reduced. Fuel ethanol was first used in the 1920s, but with the development of oil from fossil sources, ethanol was eliminated because it was not economical. However, with the increase of the price of fossil oil and the development of large-scale agriculture, more attention is being paid to fuel ethanol today, and ethanol has become an important part of the petroleum refining industry. In recent years, the average ethanol supply in the international market has increased by approximately 10% each year. As environmental pollution becomes one of the major problems around the world, ethanol fuel has attracted more attention because of its advantages over fossil fuels. It has been reported that, in the future, ethanol use will increase by more than 50% each year.

Presently, ethanol produced from corn and sugarcane has already been widely used in the United States and Brazil, respectively, and the technologies have been developed to an industrialization level. Ethanol produced from sweet potato, cassava, sweet sorghum, and maize uses approximately 8 tonnes, 7 tonnes, 15 tonnes, and 3.3 tonnes, respectively, for each tonne of ethanol produced. The cost of fuel ethanol from sweet sorghum is approximately 300–350 €/tonne. Ethanol from corn is a little more expensive, approximately 450–500 €/tonne, and the cost of ethanol from cassava and sweet potato is 400–450 €/tonne.

Sugar or starches from agriculture are the normal materials used to produce fuel ethanol. To measure efficiency of a crop for production of fuel ethanol, two factors must be considered: output and its net energy rate (NER). Some crops' NER are as follows: sugarcane 1.9–2.7, sugar beet 0.56, corn 0.74, cassava 0.69–3.56, and sweet sorghum 1.0. The fermentation yields of ethanol from various methods, as reported by researchers from other countries, are shown in Table 9.1.

LSF is the most mature technology for fuel ethanol production; therefore, it is easy to monitor and has already been used in industrial production (Xiao and Feng, 2006). For example, in a LSF process in Brazil, the yeast can be recycled three times per day. Each cycle takes 6–10 h, the ethanol concentration can reach 8–10%, and the conversion ratio can reach 92–93%. When using starch as a raw material, LSF is widely used. After saccharification, starch changed to sugars can

Table 9.1. Yield of alcohol by fermentation of different crops.

Raw materials	Land production [tonne/hectare/year]	Sugar or starch [%]	Ethanol production [L/tonne material]	Land ethanol production [kg/hectare/year]
Sugarcane	70	12.5	70	4900
Cassava	40	25	150	6000
Sugar beet	45	16	100	4300
Sweet sorghum	35	14	80	2800
Corn	5	69	410	2050
Wheat	4	66	390	4560
Rice	5	75	450	2250

be used by yeast and then changed to ethanol after fermentation. However, LSF produces a large amount wastewater, and the energy consumption is extensive. Waste water pollution in ethanol industries in China is a very serious issue (Viniegra-González and Favela-Torres, 2003), as the COD value can reach 30,000–40,000 mg/L, with a pH value of 4–5, making it very difficult and expensive and to reach the national level-1 emissions standard. Environmental pollution is one of the most important factors that restrict the development of the ethanol industry. Therefore, given the environmental protection advantages, green SSF technology is the direction of the future for the development of ethanol production.

Sweet sorghum contains a large amount of biomass and sugars (Prasad *et al.*, 2007). The ethanol production from each hectare of different types of sweet sorghum is approximately 3100–5235 L/tonne, while that from sugarcane is approximately 4680 L. Sweet sorghum can grow in semi-arid regions, and its requirements for water and nutrition are very low. Compared to that of sugarcane, ethanol produced from sweet sorghum is very clean and is the ideal material for production of fuel ethanol (Chum and Overend, 2001).

After 17 years of research, the European Community (EC) has identified two types of biomass energy: sweet sorghum and fast-growing rotation trees. However, the productivity of sweet sorghum is approximately twice that of fast-growing rotation trees, so more attention has been paid to it worldwide. Sweet sorghum research has been conducted in Indonesia, Mexico, the United States, the former Soviet Union, India, and China.

9.5.1 Sweet sorghum stalk liquid fermentation technology

The key factor of sweet sorghum stalk liquid fermentation technology is the sugar concentration. The water content of sweet sorghum stalks is approximately 65%, and the sugar content is 14–21% (Shen and Liu, 2007).

Chinese Academy of Agricultural Engineering (CAAE) has built a production-oriented LSF fuel ethanol production project in Anqiu, China, that can produce 400 tonnes of ethanol each year. Its major technologies are immobilized yeast technology and multiple continuous rapid fermentation. The results showed that: the average alcohol yield is 95% of theoretical yield; the mean residence time is 9 h; the amount of residual sugar is lower than 0.2%; the productivity is 7–11 g/L/h; and the production capacity is 720–1680 L/day.

However, this technology has many problems, such as the large amount of wastewater that is produced (10–13 tonnes of wastewater per tonne of ethanol), a production cycle that is too short (juice can be stored for less than 30 days), and sugar storage that is difficult, requiring efficient sterilization and airtight containers. The raw material utilization rate is low (45–50% of the sugar inside sweet sorghum stalks cannot be used), which limits its application and dissemination.

Zhongke Tiantian Biological Technology Co., Ltd (Baiyin, China) has performed research on the development of sweet sorghum varieties and fermentation for many years. It has already performed a series of experiments on more than 10 types of sweet sorghum in western regions

in western China and has already isolated four types of sorghum whose yield per acre can reach 8 tonnes, with a juice concentration of up to 20%. More than 9% ethanol was obtained by direct fermentation of the juice of sweet sorghum in less than 16 h.

9.5.2 *Sweet sorghum stalk SSF technology*

According to the traditional process of liquor production that use SSF, and the raw material features of sweet sorghum stalks, SSF can increase equipment utilization rate and produce less wastewater. CAEE designed and established a sweet sorghum stalks SSF project in Yuelai County, China.

This process includes a traditional "leaven pool"-type fermentation and "steamer-filling barrel"-type evaporation process for making wine. Its conversion rate from the fermentation of sugar reaches 46.3%, the alcohol yield is 8.1% (the average juice brix is 18%), and the average fermentation cycle is 3.4 days. Therefore, there are obvious shortcomings, such as the fermentation cycle is too long, the sugar fermentation conversion is too low, the labor requirement is too high, and the economic advantages are limited.

A demonstration plant for ethanol fuel production, based on sweet sorghum stalk SSF, was built in Jan 2010 in Erdos, Inner Mongolia, as a cooperative project between INET of Tsinghua University and Te Hong Biological Co., Ltd. The 127 m³ rotary drum fermentation reactor has entered the actual production stage. The test run results showed that the fermentation time was 24 h, the sugar conversion rate reached 94.4%, and the ethanol yield reached the theoretical value of 92%. This test process had positive results in overcoming the problems that have been present in sweet sorghum ethanol production technology in recent years; the process has achieved the highest level of sugar conversion rate that has been reached by SSF. The solid waste remained after fermentation can be used to produce feed for livestock through a simple process of squeezing and drying, which will create a circulation economy development model.

9.5.3 *The prospect of SSF*

9.5.3.1 *Basic theory for research*

In the SSF process, the kinetic equations of bacteria, the substrate concentration, and product concentration, and the mathematical simulation of mass and heat transfer of SSF, are the key research areas for SSF engineering, and they play an important role in industrialization and commercialization of the SSF process.

The research on the dynamics of SSF is far behind the research on LSF, predominantly because it is difficult to measure accurately the contents of microorganisms, which are the basic data sought in various projects in dynamics research. Presently, the data on the contents of microorganisms are generally obtained by the indirect method.

Mass and heat transfer in SSF remains an important focus for research in the future. The mathematical model of solid-state reactor that scholars have established is just a beginning. As a solid phase is not a continuous phase and material status is uneven, many assumptions have to be made when establishing a mathematical model. This situation causes difficulty in constructing a useful mathematical model. For example, it is generally assumed that a solid substrate is a uniformly spherical shape and that the particle clearance space is very regular. A model based on these assumptions would be very different from the actual circumstances of SSF.

9.5.3.2 *SSF reactor design and scale-up*

To solve the problems of equipment design and scale-up, the process of mass and heat transfer is still the key. The biggest problem of SSF is possibly the challenge of removing heat to keep the fermentation temperature within the range of the controlled temperature. At present, ventilation is one of the effective means to remove fermentation heat. To achieve the best effect, ventilation must be combined with stirring, while avoiding damage to the microorganisms by the shearing force caused by stirring. A way to prevent microorganisms from breakage must also be considered in a fermentation reactor.

The rotary drum bioreactor is one of the most widely used reactors. Huadin, *et al.*, using a non-dimensional design factor to study and design the rotary drum bioreactor, according to the heat generated during microbial growth and the heat removal efficiency, were able to predict the highest temperature the reactors can reach under given conditions, to obtain the maximum resistance temperature, and to construct the corresponding control measures combined with operation variables.

This method brings out three strategies when using the geometrical similarity principle for reactor design:

- Maintain a constant velocity of the air that go through the surface of the solid substance in rotary drum bioreactor.
- Maintain a stable ratio of the volume of the reactor to air in rotary drum bioreactor.
- Controlling the airflow speed in a larger-scale reactor is required to keep the highest temperature at a certain level that is the highest temperature the smaller-scale reactor can reach.

9.5.3.3 The SSF process and product contamination control

SSF can be polluted by miscellaneous microorganisms, especially in long-term fermentation. Therefore, avoiding microbial pollution is a common challenge. The main reason for pollution in the fermentation process is that it is difficult to sterilize solid material. For example, mold is a common microbial pollutant in alcohol fermentation. Some miscellaneous microorganisms cause serious problems. However, other bacteria, such as lactobacillus, acetic acid bacteria, and butyric acid bacteria, which can produce a citric acid, can cause positive effects on flavor of wine in the process of wine making because the generation of easter that is the main source of aroma requires citric acid as the substrate. Presently, the following strategies are used for controlling microbial contamination:

- Select material with low water activity to prevent bacterial contamination
- Increase the size of inoculums to prevent pollution
- Adjust the *pH* value
- Use cooling to prevent pollution
- Add salt to inhibit the growth of miscellaneous microorganisms.
- Control environmental pollution inside the incubator and ensure sterilization of facilities.

At present, the use of SSF is expanding, as different areas have different requirements on production processes and product quality control.

There is a need to develop practical and effective method to prevent miscellaneous microorganisms pollution. The specific requirements from the areas of new energy and chemical engineering should be considered in SSF equipment research and process design.

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CHAPTER 10

Optimization of biogas processes: European experiences

Anna Behrendt, Silvia Drescher-Hartung & Thorsten Ahrens

10.1 INTRODUCTION

According to the energy and climate strategies of the EU, at least 20% of Europe's energy demand should be covered by renewable energy by 2020. From 1990 until 2009, the renewable energy share of the EU energy consumption rose from 4 to 9% while the overall amount rose from 1665 Mtoe to 1703 Mtoe (European Commission, 2011). Therefore, the need to increase the application of renewable energy is still present, even though the overall energy consumption will be decreased at the same time by 20%.

Constructing biogas plants, improving fermentation and gas upgrading technology is one possibility to meet the challenge of future energy cover. Germany is one of the pioneers in the biogas field. From 2004 to 2011 the number of biogas plants rose from 2050 to 7320 and the installed capacity from 390 MW_e to 2997 MW_e (Fachverband Biogas e.V., 2012). This development can partly be credited to the renewable energy laws and subsidies in Germany for installing biogas plants with renewable energy crops. Now the trend goes towards the use of alternative biomass such as organic waste for biogas production as it does not compete with food supply. This approach is even more carbon neutral than the use of energy crops. This technology is not only interesting for Germany but for the whole of Europe, as especially in Eastern countries waste treatment has to be implemented and improved soon according to 2008/98/EC anyway.

Biogas is one possibility to produce gas as well as electricity, heat and fuel. It is storable and flexible with respect to the organic material used: energy crops, bio waste or organic by-products from industry.

In this chapter, different substrates and their basic properties are introduced together with their methane potential and energy output and technical requirements. Furthermore, current biogas technologies with regional implementation of fermenter technology and future prospects and individual regional energy solutions are presented.

10.2 SUBSTRATES FOR BIOGAS PROCESSES AND SPECIALITIES

10.2.1 *Available substrate streams for biogas processes, composition and organic amounts*

With respect to suitable substrates for anaerobic digestion processes in order to obtain biogas a widespread rethinking has taken place in the last years. Having started with manure or sewage sludge in simple reactors the spectrum of organic substrates used for biogas production has expanded. Various organic materials that accrue as by-products in industrial or agricultural processes as well as non-edible biomasses that do not comply with strict international or national food and forage regulations can be used. Additionally, depending on the national waste systems, separately collected bio waste and organic fractions from the municipal residual waste have to be considered as substrates for biogas plants. As each of these types requires certain treatment, handling and adapted fermenter technology some substrate streams are introduced in the following section to point out special characteristics. The data have been collected and analyses performed for the European funded project REMOWE (Regional Mobilizing of Waste to Energy Production)

Table 10.1. Dry matter (DM) and organic dry matter (oDM) of the substrates.

Date	Region/city	EWC code	DM	oDM
May 2010	Organic fraction Wolfenb. 40–120 mm	20 01 08	43.40	30.80
May 2010	Organic fraction Wolfenb. 8–40 mm	20 01 08	70.34	21.65
May 2011	Organic fraction Wolfenb. 40–120 mm	20 01 08	26.40	23.63
May 2011	Organic fraction Wolfenb. 8–40 mm	20 01 08	56.30	28.41
Average 2010	bio waste Wolfenbüttel	20 01 08	31.2–56.7	21.1–37.8
March 2010	Kuopio household waste average	20 03 01	39.88	24.88
April 2010	Västeras, bio waste	20 01 08	29.90	26.02
March 2011	Estonian Mix	02 07, 19 08 09, 20 01 25, 20 01 08	43.65	41.81
March 2011	Lithuanian Mix	02 01 06, 02 07 02, 19 08 05, 19 08 01, 20 01 25	20.32	18.43
April 2010	Taurage, dump waste	20 03 01	54.13	14.79
January 2011	edible fat, Estonia	200125	99.93	99.92
January 2011	brewers' grains, Estonia	0207	23.43	21.03

from March 2010 to September 2011 at Ostfalia University of Applied Sciences in Wolfenbüttel (Behrendt *et al.*, 2011a). Other data have been collected from June 2009 to May 2010 from local, separately collected bio waste and municipal waste in Wolfenbüttel, Germany.

Regarded substrate groups:

- Organic parts from municipal residual waste, fractions 8–40 mm and 40–120 mm (Wolfenbüttel, Germany)
- Separately collected bio waste, monthly analyses (Wolfenbüttel, Germany)
- Municipal waste, crushed to 30 mm and manually separated from glass, stones and metal (Kuopio, Finland (REMOWE))
- Separately collected bio waste (Västeras, Sweden (REMOWE))
- Mixture (kitchen and canteen waste, grease trap waste, edible fat, brewers' grains) (Estonia (REMOWE))
- Mixture (cow manure, screenings from sewage plant, palm oil, waste from spirit distillation, dried sewage sludge) (Lithuania (REMOWE))
- Dumped waste (Taurage, Lithuania (REMOWE))
- Edible fat (Estonia (REMOWE))
- Brewers' grains (Estonia (REMOWE)).

10.2.1.1 Water and organic matter concentration

As can be seen in Table 10.1 the dry matter and organic dry matter content of the selected substrates varies from low organic content as in dumped waste or liquid material, to high values as in edible fat. The water content also varies a lot and indicates similarly that the different materials need their individual treatment.

Figure 10.1 shows the monthly distribution of the DM and oDM for bio waste in the Wolfenbüttel region. As the bio waste also contains large amounts of garden waste it can clearly be seen that oDM rises after a dry summertime and reaches its peak in January with a high content of Christmas trees. The bio waste generation reaches its minimum in the spring months. Other types of waste are disposed with the bio waste and have to be sorted out at the composting sites.

10.2.1.2 Requirements for pretreatment including sorting and sanitation

To obtain optimal biogas output out of organic material, the substrate composition, no matter if it is organic waste or energy crops, has to be suitable for the fermentation technology. Therefore,

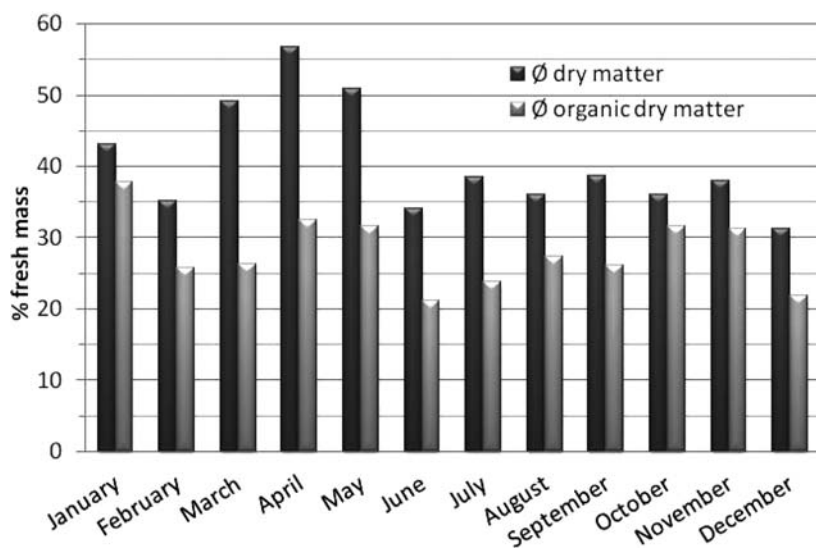


Figure 10.1. Monthly figures of bio waste dry matter and organic dry matter development.

especially in case of residual organic wastes a compatible pre-sorting has to be introduced. It has to be as simple as possible to avoid process failures due to complex layout, also it has to be as effective as possible and at the same time energy-saving. If the fermenter is a lab-scale application, the accurate pre-sorting is even more important than for large-scale biogas plants as the relation between substrate size and plant size is smaller. In 2011, several anaerobic continuous tests with different substrates in 15 L lab scale reactors were performed in the laboratories of the IBU (Behrendt *et al.*, 2011b). In Figure 10.2, photos of the stirrers inside the reactors are shown. The respective tests were running with household waste from Kuopio, Finland, already crushed to 30 mm and presorted manually by the lab staff. Nevertheless, fibers, plastics and wood pieces adhered to the stirrer and at the bottom of the reactors sand, stones and glass accumulated. Both phenomena disturbed the mixture quality of the process and reduced digestion capacity inside the fermenters.

Both can also take place in large-scale biogas plants if the material is polluted and the plant does not fit the material. If the reactor tanks cannot be cleaned during the fermentation process or sedimentations cannot be drained from the reactor bottoms, the plant efficiency will decrease significantly over time. In addition, the scaling, fouling and deforming of stirrers can cause great efficiency losses. If the stirrers cannot work reliably and the substrate is inhomogeneous, as is possible in organic waste or organic fractions in waste, a layer forming can appear. Figure 10.3 shows the example of layer forming in lab-scale fermenters fed with household waste.

Pre-sorting of organic substrate is useful if the material is fed into an already existing biogas plant, which needs a special type of input material. When plants are expanded, a pre-sorting module should be added. In Figure 10.4 an example of the influence of sanitation on the methane production process is shown (for further details on process description see section 10.2.2.1). Bio waste was fed for 14 weeks into two continuous reactors and the substrate was sanitized at 55°C for 10 h or 70°C for 1 h.

The average methane output of batch fermentation processes is approximately 560 Nm³ (CH₄)/Mg (oDM). Reactors 1 and 2 showed a very similar development of the methane production. The results of the continuous tests did not correspond to the batch test results which should present the maximum possible amount of methane production but they came close.

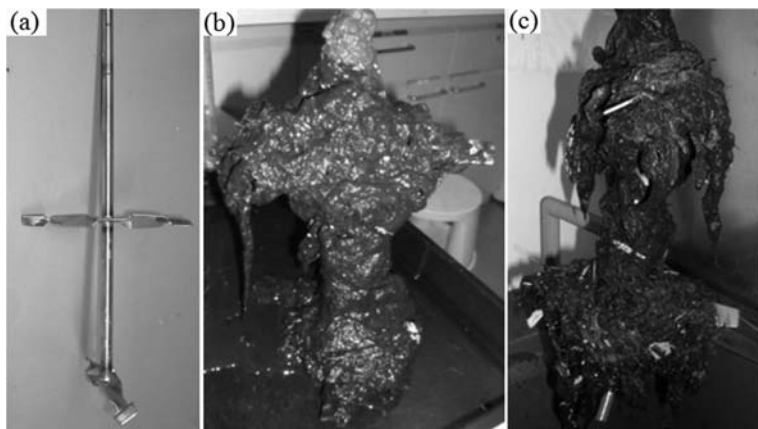


Figure 10.2. Mixed household waste, Kuopio, reactor 1 stirrer: (a) originally (b) after three-month testing period, (c) after rinsing with water.

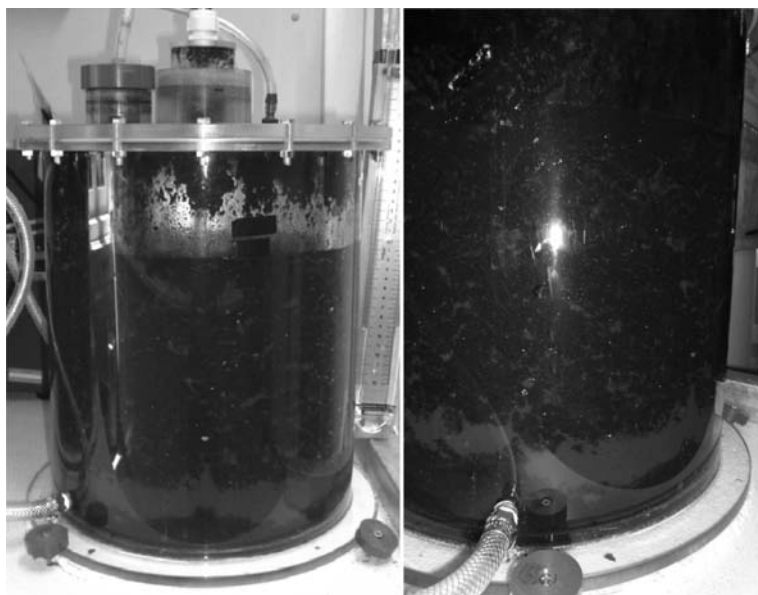


Figure 10.3. Layer forming in mixed household waste reactors.

From week seven on the sanitation changed and this can be an explanation why the methane production rose. The substrate could be digested more easily but the process itself has been more difficult to handle.

10.2.2 Biogas potentials and energy output

10.2.2.1 Identification of biogas potentials

To gather anaerobic fermentation data two basic steps were performed. On the one hand, batch fermentation tests to determine the maximum biogas potential of each substrate, and on the other hand continuous tests to measure the long-term fermentation behavior of individual substrates and

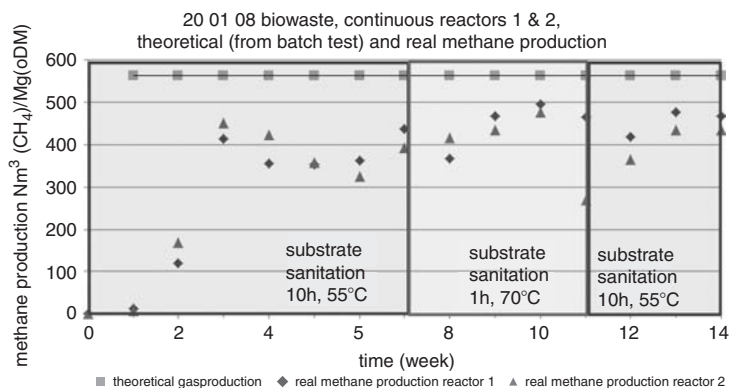


Figure 10.4. Results of continuous biogas fermentation tests.



Figure 10.5. Batch tests in a heating cabinet.

substrate mixtures were performed in lab-scale. The batch tests were performed in 5 L Erlenmeyer flasks, with rubber plugs, valves, a Thesseraux[®] gasbag and some pipe devices according to VDI 4630 *Fermentation of organic materials*. The batch reactors were placed under mesophilic conditions in heating cabinets at 40°C for 35 days as can be seen in Figure 10.5. The inoculum, usually sewage sludge, was mixed with the substrate in a certain ratio and the oxygen was removed from the reactors by flushing them with nitrogen before the plug and gasbag were connected. During the 35 days reaction time in the heating cabinet the reactors were shaken daily and gasbags were measured with respect to volume and gas composition whenever 2 L gas or more was produced. A detailed description can be found in REMOWE final report O3.2.3.1 (Behrendt *et al.*, 2011a).

10.2.2.2 Biogas potential results and energy output

The bioreactors produced biogas during the 35 days testing period and the gas composition and volume was measured occasionally. After finishing the tests, the methane amount was applied to the amount of fresh mass or organic dry matter. Table 10.2 shows results for methane potentials of the selected substrates.

Table 10.2. Methane potential of the substrates.

Date	Region/city	Nm ³ (CH ₄)/Mg (fresh mass)	Nm ³ (CH ₄)/Mg (oDM)
May 2010	Organic fraction Wolfenb. 40–120 mm	95.5	310.20
May 2010	Organic fraction Wolfenb. 8–40 mm	49.3	227.80
May 2011	Organic fraction Wolfenb. 40–120 mm	172.1	606.00
May 2011	Organic fraction Wolfenb. 8–40 mm	62.15	263.00
Average 2010	biowaste Wolfenbüttel	35.8–79.0	114.8–233.7
March 2010	Kuopio household waste average	69.4	286.7
April 2010	Västerås, biowaste	146.8	564.0
March 2011	Estonian Mix	259.8	621.4
March 2011	Lithuanian Mix	85.2	462.2
April 2010	Taurage, dump waste	18.7	126.6
January 2011	edible fat, Estonia	745.0	745.6
January 2011	brewers' grains, Estonia	93.8	446.3

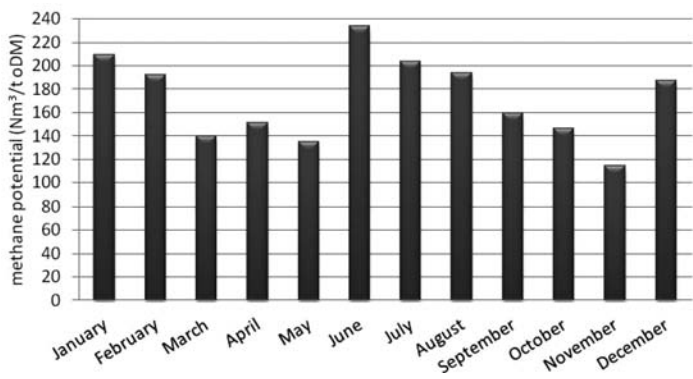


Figure 10.6. Bio waste monthly methane potential after a 35 days fermentation period.

The results for the substrates analyzed in the REMOWE project showed good tendencies regarding methane potentials. Old waste that had been dumped for at least six months only shows low methane output. Fresh household waste only a couple of days old, as e.g. the samples from Kuopio, show higher methane potentials. The other REMOWE substrates shown in Table 10.2 show very good methane potentials as already indicated by the promising substrate compositions.

As already indicated in section 10.2.1.1, the existing seasonal diversity concerning the organic matter also affects the methane potential, see Figure 10.6. In comparison to the November values, the June results are almost double. Therefore, thinking about anaerobic digestion instead of composting has to be considered carefully as the methane outcome cannot just be averaged annually without taking into consideration the seasonal distribution. In addition, there is no direct correlation between the oDM and the methane potential. The prediction of the actual methane potential in biogas plants therefore has to be pre-tested in lab-scale continuous fermentation tests.

In addition, the differences from 2010 to 2011 in the organic fraction of municipal household waste from Wolfenbüttel shows that a well-prepared data basis is necessary before a reliable statement can be made. Nevertheless, the tendency of higher methane potentials in the 40–120 mm fraction compared to the 8–40 mm fraction is supported.

Depending on the substrate, this phenomenon of seasonal dependency points out that this aspect might also have to be considered for other materials. Planning a biogas plant for organic substrates other than energy crops requires attention.



Figure 10.7. Continuous lab fermenter.

Before starting the continuous digestion tests, the 15 L reactors had to be established (Fig. 10.7). Acrylic glass reactors with a self-constructed stirring device were used. A modified drill machine was installed at each reactor with a revolution of 100 rpm (1). On top of the reactor were several ports.

The first port (2) in the center is the water seal to guarantee a stirring without inserting air into the anaerobic process. Furthermore, a water seal can prevent damage by overpressure inside the fermenter (also digester). The two smaller ports are for collecting the produced gas in special gasbags from Tesseraux® (6). The last port (5) is the sampling port, where samples were taken or substrate fed. To get an optimal temperature of 40–42°C for digestion the fermenter has a double-walled heating coat (3). Water is heated by a water bath and pumped into the heating coat of the reactors.

The reactors were filled with 12 L sewage sludge and heated up to 40°C. The fermenters were fed Monday to Friday and samples were taken out on demand for analysis and to keep the fermenter load leveled. In the first weeks, the organic load was increased whenever the process showed stable biogas production and acceptable buffer capacity.

The following analyses were done daily (d) or weekly (w):

- determination of VOA/TAC value buffer capacity (d, w)
- pH-value (w)
- conductivity (w)
- amount of produced biogas (d)
- comparison of produced biogas (d)
- ammonium, phosphate, nitrogen concentration (w)
- dry matter and organic dry matter (DM/oDM) (w)
- organic acids concentration (w).

Beside these analyses a daily inspection of the reactors, stirring devices and water seals concerning functionality and tightness is necessary.

Table 10.3. Test parameters and methane potential results from continuous fermentation tests.

	Estonia	Finland	Lithuania	Sweden
Substrate	brewers' grains, edible fat, bio waste, grease trap waste	municipal household waste	cow manure, sewage sludge, screenings, spirit distillation waste, palm oil	biodegradable kitchen & canteen waste
Pre-sorting	—	✓	—	—
Testing period [d]	86	120	127	106
Range of organic load	0.7–2.1	2.1–4.9	1.26–3.5	1.4–3.5
Sanitation 10 h, 55°C	—	—	✓	✓
Sanitation 1 h, 70°C	—	✓	—	✓
Effects through sanitation	—	✓	✓	✓
Average stable methane production [NL/h]	0.9875	0.5026	0.5725	1.2096
Average buffer capacity	0.12	0.13	0.25	0.19
Methane output [Nm ³ (CH ₄)/Mg oDM]	691.7–739.6	183.1–345.4	369.5–479.9	365.9–476.9

The continuous tests run for at least three months in order to analyze long-term effects of substrate behavior in the biogas process. For the REMOWE project the following key data are available (Table 10.3). Detailed results can be found in the REMOWE final report O3.2.3.1 or O3.2.3.2.

10.2.2.3 Comparison of energy outputs through biogas and combustion of material

The comparison of energy outputs through biogas and combustion of materials relates more to the question how much energy is left in the fermentation residues and if it is worth the effort to gain the additional energy.

Some of these issues are relevant for all substrates that have been examined at the laboratories of Ostfalia University of Applied Sciences, Wolfenbüttel. Before the digestate can be transported to the place of destination, the residual gas potential has to be regarded. First, it gives information about the functionality of the fermentation process itself; if the residual gas potential rises quickly, something is malfunctioning.

The emission of harmful CH₄ to the atmosphere is the second problem that has to be avoided. And of course, the energy yield should be as high as possible. To get an insight into the energy potential of the leftover digestate, calorific tests were performed with all digestates from the lab-scale tests.

The heating value is the maximum amount of usable heat quantity that is produced by combustion. The heating value, also calorific value, includes the condensation of water vapor, therefore the calorific value is higher than the net calorific value. Thus, the heating value is a degree of usable heat quantity with heat of condensation.

The heating value is specified in relation to mass e.g. kilojoules per kilogram (kJ/kg). To measure the heating value, traditionally a bomb calorimeter is used. The bomb calorimeter is used with oxygen ambiance under high pressure. For this, a steel container (bomb) is embedded into tempered water and is assumed as an adiabatic system. The measured sample is placed inside the bomb in a special crucible and ignited through an ignition wire. Through measurement of the heat, the heating value can be calculated. There are several measurement principles for heating value determination.

Through detection of temperature increase during the incineration of substrate, the heating value can be determined. Water, which is inside the sample, and water that is produced during

Table 10.4. Digestate energy content according to calorific tests.

	Finland	Lithuania	Sweden
Average methane production from lab-scale [Nm ³ /t oDM]	275.47	406.85	453.83
Annual substrate amount [t/a]	20,000	606894	14000
Substrate oDM [%FM]	31.78	18.43	26.02
Energy content CH ₄ [kWh/m ³]	9.94	9.94	9.94
Annual energy from biogas [MWh/a]	17403	452333	16432
Annual digestate amount* [t/a]	17000	515859	11900
Digestate DM [%FM]	13.17	6.41	5.92
Heating value [kWh/kg DM]	3.903	4.933	3.946
Annual energy from digestate [MWh/a]	8738	163117	2780
Percentage digestate energy of biogas energy [%]	50.2	36	17

*digestate = 85% of substrate amount.

the incineration, is condensing so the reaction is running isochoric. The following formula shows how the heating value is calculated:

$$HV = (C \times \Delta t - (Q_z))/m_p$$

where:

C = heat capacity of calorimetric system $C = 9756.25$ J/K

Δt = increase of temperature of calorimetric system

Q_z = amount of all external heat which does not count in the measured sample
(e.g. heating value of ignition wire)

HV , wire = 7411.76 J/g (manufacturers' instructions).

Results of the tests can be found in Table 10.4, excluding data for Estonia due to lack of information concerning the annual substrate generation.

The values in Table 10.4 show that, depending on the substrate, the energy potential in the digestate is varying from 17 to 50% depending on the biogas potential. Another possibility would be the combination of digestate combustion and fertilizer use. Therefore, the sole heating value from solid parts of the digestate has to be further analyzed.

10.2.3 Conclusion: can energy from waste compete with energy from renewable products?

The current suitability of waste for biogas production depends on the effort to build the fermenter with all necessary infrastructures, the willingness to invest in the setup, and the need for alternative and renewable energy. It has to be stated that if working with waste streams, the different needs concerning pre-sorting, sanitation or disposal of the digestate have to be considered and not only the sole methane yield is important. The waste has to be used soon after the time of production. The water content in the substrate has to be considered when thinking about the fermenter technology to gain maximum energy efficiency. The seasonal composition of household and organic waste has to be considered when thinking about covering energy needs. In addition, according to the input material the process stability has to be guaranteed, even though substrate composition may vary.

10.3 CURRENT BIOGAS TECHNOLOGIES AND CHALLENGES

10.3.1 Biogas fermenter technology

For biogas production by anaerobic fermentation, different kinds of processes exist. The possible types of processes are summarized in Table 10.5.

Table 10.5. Classification of methods for biogas production using different criteria (FNR, 2009a).

Criteria	Distinction
• Number of process stages	• single stage • two stage • multi-stage
• Process temperature	• psychrophilic • mesophilic • thermophilic
• Feeding process	• discontinuous • semi-continuous • continuous
• Dry mass content of the substrate	• wet fermentation • dry fermentation

Table 10.6. Biogas process (Weiland, 2007, adapted).

Wet fermentation 8–10% DM _{ferm}	Dry fermentation > 30% DM _{sub}
• continuous process • for liquid, pasty and solid substrates • good material and energy exchange • safe gas delivery	• discontinuous/continuous process • for stackable substrates • no mixing • small reaction volumes • high loading rates

Single stage plants do not have a spatial separation of the different phases of the digestion process (hydrolysis, acidification, acetic acid formation, methane), and there is only one fermenter.

Two or multi-stage processes have different fermenters where the different phases of the process take place.

Mesophilic biogas plants work at a temperature between 32 and 38°C, thermophilic plants between 42 and 55°C. The limits, however, are floating (e.g. due to individual adaption phenomenon or microsphere material transportation effects).

The feeding of the plants is carried out continuously, semi-continuously or discontinuously. For the discontinuous feeding, there are two kinds of processes, the batch process and the exchangeable container process (garage process, container process). The discontinuous feeding carries most weight in dry fermentation.

The semi-continuous and continuous processes are distinguished according to the flow method, storage method and the combined storage-flow method. In contrast to the continuous feeding, at the semi-continuous method an unfermented charge is carried into the fermenter once a day at least (FNR, 2009a).

The output of a biogas plant depends on the used substrate and the size of the fermenter.

An overview of the dry digestion and the wet digestion process can be found in Table 10.6 and the advantages and disadvantages of both methods are summarized in Table 10.7.

10.3.1.1 Dry digestion application – Examples of biogas plants in Germany

The dry digestion technology normally uses organic waste or renewable materials and also residual waste as substrates with a dry mass content of 25–30%. The substrates are difficult to pump. Therefore dry digestion is especially suitable for such plants, which do not have additional liquid manure available. The loading rate of the fermenter is at least 3.5 kg oDM/m³/d. (Renewable Energy Concepts, 2012). The process is adapted for continuous, semi-continuous or discontinuous

Table 10.7. Advantages and disadvantages of dry and wet fermentation (Weiland, 2007, adapted).

Dry fermentation		Wet fermentation	
Advantage	Disadvantage	Advantage	Disadvantage
• Small reactor volumes • Low heat demand • No formation of floating and sinking layers • Insensitive to contaminants • High space-time yields	• Higher investment costs • Limited to dry substances • No co-processing of liquid substrates	• Good material and energy exchange • For liquid and solid substrates • Reliable gas delivery • Application of the digestate with low emission	• Large reactor volumes • Large material flows because of recirculation of percolate • Risk of inhibitor concentration • Risk of floating roofs

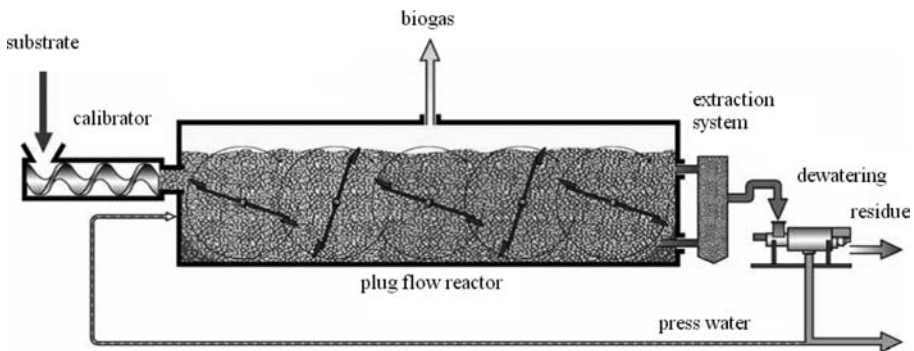


Figure 10.8. Process flow diagram: plug flow fermenter (STRABAG, 2012, adapted).

operation and thus different types of biogas plants are available. In the following, some different types of biogas plants reflecting the current state of the art in Germany are described.

10.3.1.1.1 Plug flow fermenter

This example of a biogas plant (Fig. 10.8) works with a plug flow fermenter, operated at $\sim 55^{\circ}\text{C}$. A mixer transports the material through the elongated rectangular fermenter. The substrate which is used in this biogas plant is mainly corn silage and grass silage (Biogasanlage Kaltenweide, 2009).

10.3.1.1.2 Tower fermenter

The biogas plant in Figure 10.9 is currently the only tower fermenter operated with renewable materials, a substrate mix of whole crop silage, total plant cereal silage, sunflower silage, grass silage and poultry manure at a temperature of about 55°C (De Baere, 2010). The substrate does not require mechanical mixing inside the bioreactor, because it is already mixed outside of the fermenter (FNR, 2009b). A similar tower fermenter exists which is operated with residual waste from households ($<40\text{ mm}$) at a temperature of about 55°C .

10.3.1.1.3 Garage fermenter

Organic waste from households and other origins is fermented at a temperature of $37\text{--}39^{\circ}\text{C}$. The fermenters are fitted over the front doors, the process water which is draining off is collected, stored and, if required, trickled onto the substrate from the top of the fermenter (Abfallwirtschafts-Gesellschaft mbH, 2009). The process flow diagram of an exemplary garage fermenter is shown in Figure 10.10.

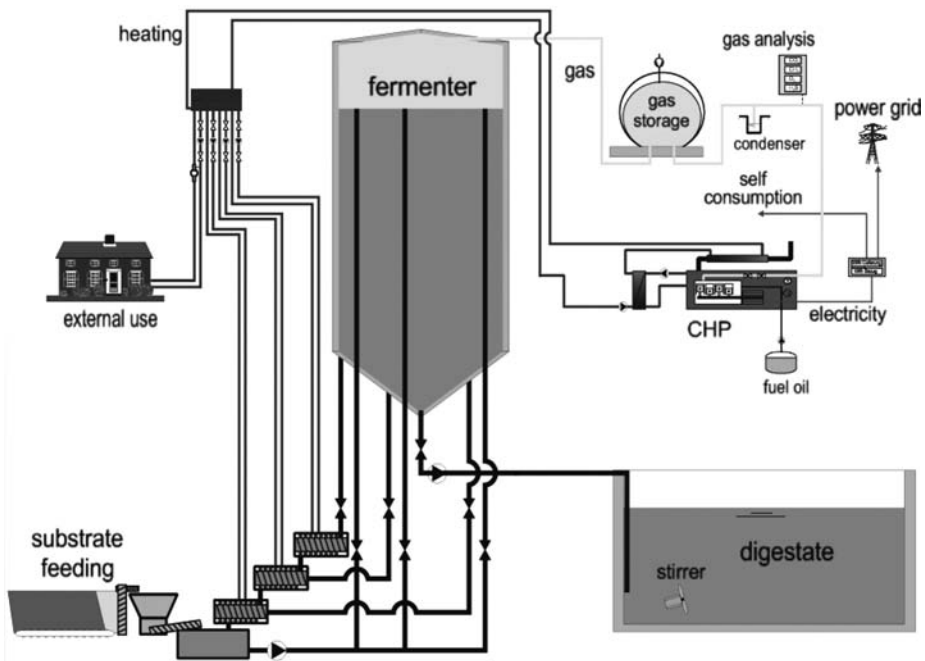


Figure 10.9. Process flow diagram: tower fermenter (FNR, 2009b, adapted).

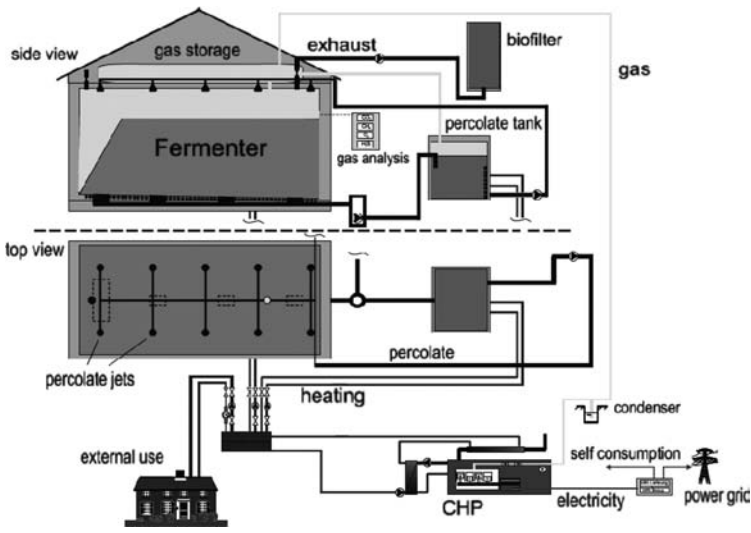


Figure 10.10. Process flow diagram: garage fermenter (FNR, 2009b, adapted).

10.3.1.2 Wet digestion applications

Wet digestion is the most common process for biogas production in the agricultural sector. The fermenter content has a dry mass of 8–10% (Weiland, 2007), and the fermenter is operated with a loading rate of about 2–3 kg ODM/day/mm³ (renewable raw materials) (Bayrische Landesanstalt, 2007). Because of the high liquid content, a good nutrient and energy exchange between bacteria

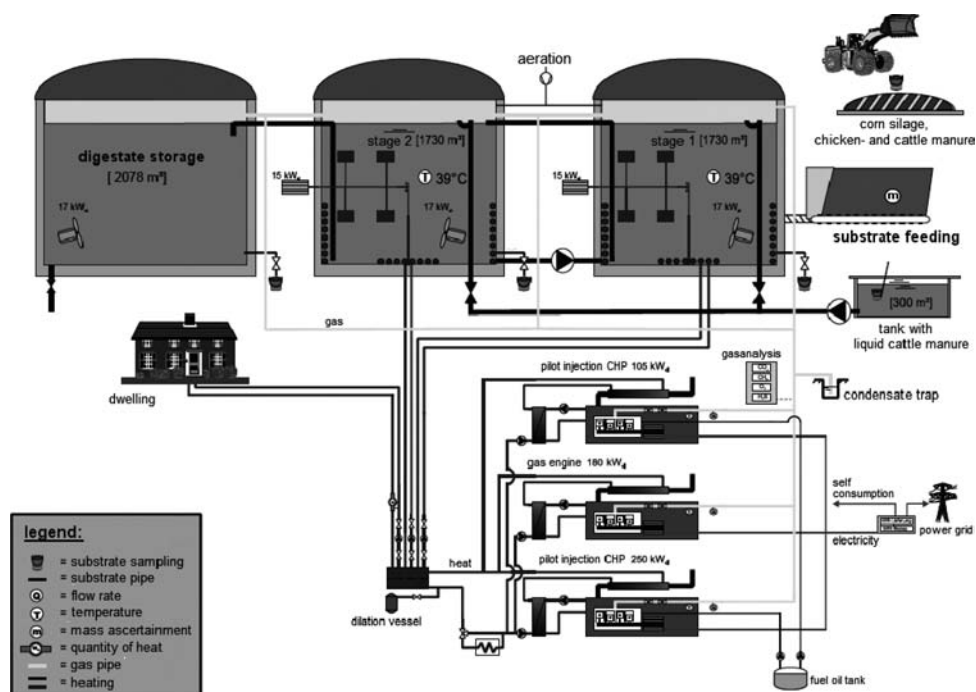


Figure 10.11. Wet fermentation plant (FNR, 2009a, adapted).

and substrate is possible (Renewable Energy Concepts, 2012). The wet fermentation is applicable for liquid and solid substrates. Due to the comparatively low dry matter content of the substrates, large reactor volumes are necessary to ensure sufficient residence time and degrees of degradation. (Renewable Energy Concepts, 2012).

10.3.1.2.1 System example

This biogas plant consists of two standing fermenters and one gas-tight fermentation residue storage tank made of reinforced concrete (see Fig. 10.11). The fermenter is operated with renewable materials (corn silage, chicken manure, cattle dung and grass silage) at a temperature of 39°C. The substrate is conveyed into the fermenter with a horizontal screw conveyor over a solid entry with walking floor (FNR, 2009b).

10.3.1.2.2 Use of residual waste

The use of residual waste as a substrate for biogas plants constitutes special procedural challenges. The pre-treatment of the material is a very important requirement. The wet fermentation of the residual waste constitutes one possibility for the fermentation of waste, but for this plant system, problems arise especially for the mixing system because of the contaminants. Dry fermentation with the waiver of mixing could avoid these problems and in addition, the expensive pre-treatment would be no longer necessary. On the other hand, the use of existing pumps might be difficult. In both kinds of fermentation, toxic contaminants are very dangerous for the microbiology and therefore the process itself (Schumacher *et al.*, 2011).

10.3.1.3 Laboratory scale technology

Based on various student project works, several layouts for dry digestion biogas plants in laboratory scale were designed.

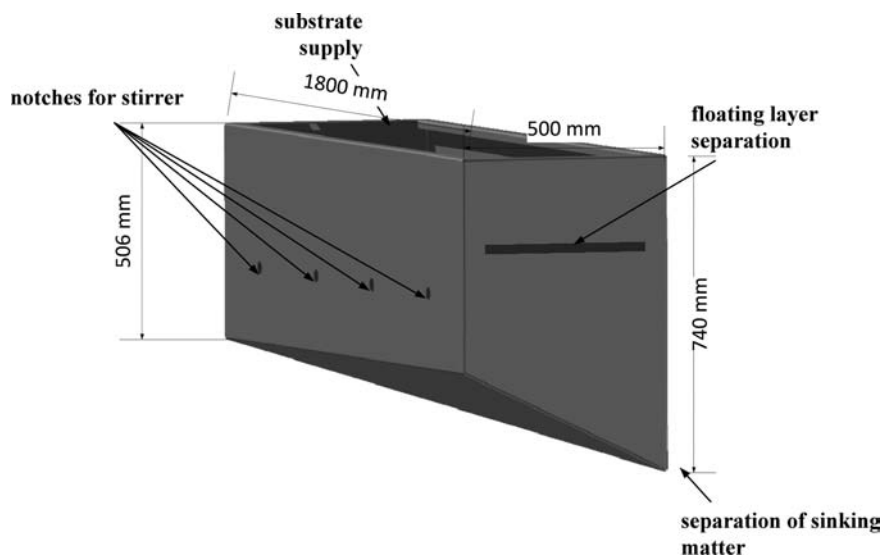


Figure 10.12. Folded fermenter sheet (Gotthold *et al.*, 2011).

10.3.1.3.1 Plug flow fermenter

Because of the special requirements for the use of residual waste in biogas plants, the idea of a plug flow lab-scale fermenter arose. The fermentation of household waste is associated with an expensive treatment of substrate. Therefore, some special plant sections are necessary. In the following, the most important parts of the fermenter are described. For the lab fermenter (Fig. 10.12) a separation of the floating layer was planned. This fraction will be separated by a rectangular plate, which is attached to the fermenter wall. The sedimenting substances are collected in the funnel-shaped ground of the fermenter, which ends in a tube to which a valve is attached. For homogenization and propulsion of the fermenter contents, slow-rotating horizontal stirrers were selected. Four of the slow-rotating horizontal stirrers are distributed on the long side of the fermenter. The fermenter will be covered by a plexiglas window, so that it is possible to look inside during the fermentation process (Gotthold *et al.*, 2011).

10.3.1.3.2 Garage fermenter

The second lab-scale fermenter, which has been planned and is currently under construction, is a garage fermenter. Because of the special challenges which are caused by the operation of current garage fermenter systems, it was the task to optimize the opening of the fermenter for the new charging. While charging the garage fermenter, remaining methane leaks into the atmosphere and huge amounts of digestate are needed for inoculating the new batch. These are two significant disadvantages. Additionally a better use of the percolate should be achieved (Cassebaum, 2012). Therefore, a lab garage fermenter (Figs. 10.13 and 10.14) is being built, which is going to be operated with different kinds of input material (renewable raw materials, biodegradable waste or residual waste). The percolate should be cultivated in an enclosed packed bed column to increase the quantity of the bacteria, which supports the inoculation of the fermenter (Cassebaum, 2012).

10.3.2 Regional implementation of fermenter technology

Waste from households, which means residual waste or organic waste, might have a huge potential for energy production. As a regional example, the use of organic waste and residual waste (organic fraction) as input material for biogas plants in Kiili Vald, a region in Estonia, is described in the following section.

Table 10.8. Theoretical coverage of Kiili Vald energy demand from a biogas plant.

	Thermal energy	Electric energy	Total
Energy demand	2200 MWh	1500 MWh	3700 MWh (100%)
Energy production (example of a calculated biogas plant)	423 MWh	210 MWh	633 MWh (17%)

At the present time, the energy sector in Estonia is dominated by the combustion of fossil fuels. Because of the existence of oil shale, Estonia is relatively independent of external energy supply. Approximately 66% of the required annual amount is covered by the country itself. About 90% of the energy production is generated by the combustion of oil shale and heavy oil from oil shale. The remaining 10% is from the renewable sector, mainly the burning of biomass but also hydroelectricity and wind energy. In addition, gas (34%) is imported from Russia (Turnhöfer *et al.*, 2011). When joining the EU in 2004, Estonia committed to increase the use of renewable energies by 5.1% of the gross energy consumption by 2010. The country also had to decrease the CO₂ emissions by 8% between 2008 and 2012 compared to the year 1990 (Turnhöfer *et al.*, 2011). In order to achieve its stated objectives, a policy was decided on energy taxation in order to promote the use of biofuels.

Kiili Vald is a small region in Harju County, the capital city Tallinn is also located in Harju County. Kiili Vald has a total area of 100.4 km² and 4182 inhabitants (World News, 2012).

10.3.2.2 The waste management situation in Kiili Vald

The quantity of municipal waste in the region Kiili Vald in 2010 was around 860 tonnes. 170 kg of waste are produced per capita (Kriipsalu, 2011), which is much less than the European average of about 513 kg per person (in 2009) (EU-Abfallstatistik, 2011). Additionally, Kiili Vald collects about 5 tonnes of biodegradable waste, 43 tonnes of packaging waste and 23 tonnes of waste paper, which is collected separately (Kriipsalu, 2011). Although the composition of the municipal waste in Estonia is not well documented, it is assumed that the waste contains a high amount of organic fractions (Kriipsalu, 2011). In rural areas like Kiili Vald, organic waste from the domestic sector in general is treated by home composting. Therefore, the potential of organic waste amounts to approximately 688 tonnes per year and 5022 tonnes of manure. In addition there are organic wastes from local food establishments and biomass like farming refuse, grass and wood (not for fermentation) (Kriipsalu, 2011). Because of the biomass potential from the theoretical planning of a biogas plant according to the outcomes of a student's project work in 2011, we expect an energy production of about 423 MWh thermal energy and 210 MWh electric energy (Padberg *et al.*, 2011).

It would be possible to cover up to 17% of the energy demand in Kiili Vald: this equals 2200 MWh thermal energy and 1500 MWh electric energy (Kukk, 2011), from a biogas plant (Table 10.8).

Table 10.9 shows the resulting theoretical energy flow of a biogas plant which is operated with organic waste, cattle manure and pig manure, using the existing data and the amount of waste produced.

By the capturing and the separate treatment of organic waste, the organic components in municipal waste are reduced, and so also a crucial step is taken in implementing the requirements of the EU Landfill Directive (99/31/EC) to reduce the proportion of organic waste in landfills. By implementing the use of renewable energies, new jobs would be created. This would be a possibility to compensate for expected job losses due to future changes in mining.

Furthermore, oil shale combustion causes extremely unhealthy dust emissions, which lead to high resulting costs in the health system. Also the land use through oil shale mining and ash landfills, and the high dependence on a limited supply of energy could be mitigated by the gradual

Table 10.9. Energy flow of the exemplarily calculated biogas plant (Padberg *et al.*, 2011), (ATB, 2012).

	Energy
Methane yield	89428 m ³
Theoretical energy value	894288 kWh
Thermal power (82%)	733316 kWh
Energy loss – waste heat (18%)	160971 kWh
Steam and heat (6%)	53657 kWh
On-site needs	
Steam and heat (47.3%)	423000 kWh
Sale	
Electric power (5.2%)	46502 kWh
On-site needs	
Electric power (23.5%)	210157 kWh
Sale	

reduction of oil shale combustion by generating energy from renewable energy sources (Padberg *et al.*, 2011).

The establishment of biogas plants would represent a significant solution to solving the problems, which arise from residual waste, if it is used as input material.

The sorted disposal of the residual waste and the use of the produced energy of biogas plants might contribute to a significant improvement in the living standards for the citizens of the affected countries.

This calculated example of a biogas plant would provide a rough estimate only. For the detailed planning of a biogas plant, there are many additional factors which have to be taken into account. For example, it is of high importance that the daily amount of the substrates is sufficient (here, yearly amounts were considered). In addition, the transport of organic waste from other regions (e.g. Tallin) may be considered. Moreover it is highly important which kind of fermentation process performs best and how the end-use of the digestate has to be organized.

10.3.2.3 The waste management situation in Germany

Since 2005 the deposition of untreated waste has been forbidden in Germany (Regulation on Landfills and Long-time Storage – DepV). Municipal wastes and other wastes with biodegradable components have to be treated by thermal or mechanical-biological waste treatment processes before deposition. Biogenic wastes have been collected separately for about 20 years. In 2008, about 13.04 million tonnes of biogenic wastes were composted in composting facilities or fermented in biogas plants. These biogenic wastes are wastes from households, gardens and parks and also from food processing, restaurants and commercial kitchens and some residues from agriculture.

About 3.85 million tonnes of the biodegradable waste were collected by public and private waste disposers. About 90% of this waste was composted and 10% was fermented in biogas plants. According to a study by the Federal Environment Agency (UBA), 85 biogas plants in which biodegradable wastes from households and trade as well as garden and park wastes were used as substrates. The amount of garden and park wastes was 4 million tonnes in 2008 (Umweltbundesamt, 2012). In 2010, German residual waste was treated in 30 mechanical-biological waste treatment plants (MBA). Of these plants, 18 had only a rotting stage, and 12 of them had an anaerobic fermentation step. The anaerobic fermentation improves the energy efficiency and the carbon footprint of these waste treatment plants because of the higher gas yields (Ketelsen, 2011).

Overall 7320 biogas plants with an installed electrical capacity of 2997 MW were in operation in Germany in the year 2011 (different technology and input material) (Fachverband Biogas e.V., 2012). By the year 2020 the number of biogas plants is expected to reach about 10,000 plants (Trend: Research GmbH, 2011).

The EEG (renewable energy law) rules that the share of renewable energies in electric energy consumption should be 35% at the minimum by 2020 at the latest (BMU, 2012).

10.4 FUTURE PROSPECTS AND INDIVIDUAL REGIONAL ENERGY SOLUTIONS

10.4.1 *Central and local biogas plants*

For the production of biogas, there are different types of system concepts e.g. central or decentralized. In the following, some different types of possible system concepts are described.

10.4.1.1 *Individual farm plant*

A typical individual farm biogas plant in Germany has a maximum electrical power of 500 kWh_{el}, and the electrical efficiency is at about 38% (8000 operating hours). Characteristically, a thermal heat utilization rate of about 15–30% is obtained, e.g. for stables and residential buildings. The substrate comes from a catchment area of about 5–10 km around the biogas plant, the application of the digestate is *in-situ* (Ökoinstitut e.V., Institut für Energetik und Umwelt, 2007). In addition, the use of the thermal energy is possible in the direct vicinity of the plant (including ORC, see section 10.4.2).

For the construction of new biogas plants, the EEG (renewable energy law) in Germany stipulates minimum requirements. Every biogas plant has to prove 60% thermal use or 60% manure use, or it has to prove direct marketing. It is no longer sufficient to produce electricity only (BMU, 2012).

10.4.1.2 *Biogas parks*

In a biogas park, several biogas plants are operated at one location. The electrical power of one plant can be the same as in an individual biogas plant (500 kWh_{el}). This equals the technical data of a single plant. A typical number of plants could be e.g. 40 (biogas park in Mecklenburg-Western Pomerania/Germany). Because of the higher amount of heat, the possibilities for the use of the heat are better (Ökoinstitut e.V., Institut für Energetik und Umwelt, 2007). The thermal heat which is produced by the biogas plants can be used for heating, local cooling, drying (production of pellets from the digestate) and also for steam generation.

The advantage of a biogas park is on the one hand the higher energy production (per engaged substrate), because of the higher amount of hours of operation. On the other hand, there are also disadvantages, e.g. because of the higher demand for substrates, the catchment area for the sourcing of substrates is larger than for single plants. Thus, the transport routes are increasing (Ökoinstitut e.V., Institut für Energetik und Umwelt, 2007).

10.4.2 *Biogas use*

Biogas can be used in many ways e.g. for decentralized power and heat production, distribution over heat networks, feeding into the gas grid or use as fuel.

In the case of biogas supply with distributed energy production, biogas is produced at a central location and largely fed into the natural gas grid after its preparation. A part of the biogas is used for the operation of a thermal power station at the location of the biogas plant. The heat loss of the thermal power station is used for the demand for process heat at the biogas plant and also for more consumers in the vicinity of the plant. The produced power is fed into the grid. The rest of the biogas could be used in more thermal power stations, which are installed at decentralized

locations where the heat is needed (Ecologic, Institut für Internationale und Europäische Umweltpolitik, 2012).

Presently most of the produced biogas is directly converted into electricity at the place of origin. In combined heat and power plants (CHP) combustion engines are operated on biogas. The combustion engine runs a generator for the production of electric power. It is also possible to operate the generator with other kinds of engines and gas turbines or to produce power with fuel cells. The thermal energy, which is generated when operating a thermal power station, is used for the heating of the fermenter (20–40%) and also for the heating of buildings or other applications (50–55%). A part of the thermal energy could be used through ORC-technology which means an organic Rankine cycle. Here the heat loss vaporizes an organically working fluid, which runs a turbine, and a generator produces electric power. It is also possible to use the heat loss of the thermal power station for cooling of stables and milk on farms and also for cold storage houses. Another possible use of biogas is in micro-gas grids, which transport the raw biogas that is not used directly at the location of the plant, to satellite CHPs. Therefore, the raw biogas has only to be desulfurized and dried.

Biogas can also be used as a substitute for natural gas. Therefore, it has to be heavily conditioned to reach the quality of natural gas. The conditioned biogas (bio natural gas or biomethane) can be used everywhere, where natural gas is used. Sweden and Switzerland were forerunners in using biogas as fuels in cars, buses, trucks and rail cars (FNR, 2012).

10.5 QUESTIONS FOR DISCUSSIONS

- What kind of influence does the substrate composition have on pre-treatment strategies?
- What has to be considered when thinking about seasonal variations of organic substrates?
- Which influence does sanitation have any other influence on the digestion process than its original purpose.
- Describe a simple but effective lab-scale method to determine the methane yield of organic substrates.
- What are the advantages of lab-scale fermentation tests?
- Is it useful to treat the digestate and gain energy or is it not worth the effort and what would be the best treatment option?
- Why is there a distinction between energy from waste and energy from renewable crops, and can their energy output be compared?
- Describe the differences between dry and wet fermentation and other distinctive features.
- Describe in words the process flow in a tower fermenter and the common or different aspects compared to a plug flow fermenter.
- Based on the regional implementation example for Kiili Vald, present a concept for a region of your choice and point out difficulties or challenges to be expected.
- Why did Germany have a biogas plant building boom in the last decade, and think about advantages and disadvantages of the development?
- Concentrate on future prospects of regional energy solutions and evaluate the presented solutions, and develop at least one idea of your own dealing with this topic.

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CHAPTER 11

Biogas – sustainable energy solutions in Nigeria

Adeola Ijeoma Eleri

11.1 INTRODUCTION

Nigeria is a country rich in natural resources, yet a majority of its population lives on less than a dollar a day. The economic outlook for the country is still uncertain and challenging. However, it is increasingly becoming clear that a lack of access to modern energy services constitutes a critical roadblock to poverty alleviation and economic growth in Nigeria while a majority of Nigerians lives in energy poverty. Ninety-five million Nigerians rely on biomass in the form of wood, charcoal, dung, and crop residue, as their domestic cooking fuel in traditional cooking stoves and open fires (Christian Aid, 2011). The smoke emitted from these fuels is a leading cause of indoor air pollution. According to the World Health Organization, every year in Nigeria an estimated 95,000 persons die from exposure to stove smoke inside their homes and currently it is the third largest killer of women and children after malaria and HIV/AIDS. The country experiences the highest number of smoke related deaths in Africa. Other challenges directly linked to poverty and a lack of access to modern energy services include poor health conditions, degraded environments, water scarcity, and pollution. Poverty and the challenge of the Nigerian energy sector are inextricably linked.

Energy is crucial for the sustained, economic, and technological development of any country and this is extremely important in Nigeria where only 40% of the population have access to electricity, leaving about 90 million Nigerians in the dark, literally.

The need for increased research interest in alternative and sustainable energy is underscored by the current global and national issues of climate change, deforestation, desertification, soil erosion, widespread poverty, and unequal access to the current forms of energy.

Despite that the energy policy of Nigeria has as part of its objectives a transition away from traditional biomass in the form of wood fuel and charcoal, this transition has not yet occurred. The Renewable Energy Master Plan of Nigeria, which also provides a roadmap for achieving a substantial share of the national energy mix through renewable energy including modern biomass energy, has not been implemented.

Sustainable energy in the form of modern biomass technology such as biogas technology has the potential to tackle the challenges facing Nigeria and unleash sustained socio-economic and human development in the country. Biogas technology has the advantage over other renewable energy technologies in that the production systems are relatively simple, less investment-intensive, can operate on a small or large scale in urban or rural locations with no geographical limitations.

The technology is simply a process of anaerobic digestion of organic matter such as agricultural wastes, municipal and industrial waste, and other forms of biomass. Anaerobic digestion consists of several interdependent, complex sequential and parallel biological reactions in the absence of oxygen, during which the products from one group of microorganisms serve as the substrates for the next, resulting in transformation of organic matter (biomass) mainly into a mixture of methane and carbon dioxide (Parawira, 2004).

Moreover, the technology has the added benefit of being able to address environmental challenges such as greenhouse gas emissions, indoor air pollution, poor sanitation, and deforestation.

Table 11.1. Indigenous energy resources of Nigeria.

Source	Capacity
<i>Fossil fuels (including nuclear)</i>	
Crude oil	35.5 billion barrels
Natural gas	187.44 trillion standard cubic feet
Tar sand	30 billion barrels of oil equivalent
Coal and lignite	639 million tonnes
Bitumen	42 billion tonnes
Uranium	Discovered in six states
Crude oil	35.5 billion barrels
<i>Renewables</i>	
Large hydropower	11250 MW
Small hydropower	3500 MW
Fuel wood	13,071,464 hectares
Animal waste	61 million tonnes/year
Crop residue	83 million tonnes/year
Solar radiation	3.5–7.0 kWh/m ² /day
Wind	2–4 m/s at 10 m height
Crop residue	83 million tonnes/year

Source: Draft National Energy Master Plan – 2006.

11.2 REVIEW OF NIGERIA'S CURRENT ENERGY SITUATION

Nigeria is blessed with abundant sources of energy, including oil and gas, hydro, biomass and solar energy. It is Africa's largest oil-producing country and accounts for nearly a third of the continent's crude oil reserves. Nigeria ranks second in natural gas after Algeria, and has large reserves of bitumen and lignite. Petroleum export is the mainstay of the Nigerian economy. Nigeria, though blessed with abundant sources of energy, is experiencing an enormous energy crisis. Present average electricity capacity requirement in Nigeria is estimated at about 12,000 MW while current supply stands at about 3800 MW (FGN, 2010). Private generators meet the deficit. In the household sector, about 95 million Nigerians depend on wood for their daily cooking and wood energy constitutes 90% of household energy use. Today the demand for wood far outstrips supply, resulting in rising prices and implications of this for desertification and global warming are apparent. The rate of deforestation is about 350,000 hectares per year, which is equivalent to 3.6% of the present area of forests and woodlands, whereas reforestation is only at about 10% of the deforestation rate (FGN, 2010). Despite a national policy to transition away from wood energy use, the prospects remain bleak in a country where 92% of the population lives in poverty (UNDP, 2006). Table 11.1 shows indigenous energy resources.

Nigeria's current energy planning favors centralized conventional gas-fired generation and with a rising population and increasing energy demand, this has consistently resulted in high network losses, limited energy access and energy poverty.

11.3 BIOGAS TECHNOLOGY IN NIGERIA

Biogas is a methane-rich gas that is produced from the anaerobic digestion of organic materials. It is a colorless, blue burning gas that can be used for cooking, heating and lighting. It has a heating value of 22 MJ/m³. It is odorless and can be obtained from various feedstocks such as cattle dung, poultry and piggery wastes. The use of biogas for heating and cooking has been in practice for a long time. Typically, a kilogram of cow dung yields about 0.09 m³ of biogas per day

(Sasse, 1988). The fuel value of biogas depends on its methane content, for instance a gas containing 65% CH₄ and 35% CO₂ has a fuel value of 24 MJ/m³ compared with 37 MJ/m³ for pure methane (Garba, *et al.*, 1996). Moreover, biogas has half the heating value per volume of methane gas, one third of propane and 50% more than coal gas. Furthermore, 1.0 m³ of the gas is equivalent to 2.0 kg of firewood, 0.6 L of kerosene, 0.5 L of petrol and 0.4 L of diesel (Garba, *et al.*, 1996).

According to the Energy Commission of Nigeria (ECN), work on biogas in Nigeria started after the Federal Government established the two renewable energy centers at Sokoto and Nsukka in 1982. The ECN has a 20 m³ plant which feeds on cow dung in Mayflower Secondary School, Ikenne Ogun State. Similarly a 10 m³ plant, which uses chicken droppings/cassava peels exists at NCERD Nsukka, Enugu State, Nigeria. The UNDP also has successfully introduced to Yobe, Jigawa and Kano States the floating drum and plastic balloon and tube types of biogas digesters under the Africa 2000 low technology biogas system. The UNDP also constructed for a family of 40 at Kwachiri community in Kano State, a biogas plant that uses cow dung for their daily energy needs (ECN, 2005). Furthermore, the Sokoto Energy Research Center (SERC) has constructed more than 10 biogas plants ranging from 10–20 m³ capacity across the country using different substrates such as cow dung, human excreta, piggery waste etc., with a failure rate of less than 20% (ECN, 2005). These two centers along with many tertiary institutions have been involved in biogas research activities but so far, less than 20 pilot projects on biogas have been established across the country (ECN, 2005).

One outstanding biogas project in Nigeria is the Cows-to-Kilowatts project. This project is a joint venture among the Nigerian branch of the Global Network for Environment and Economic Development Research, a nongovernmental organization (NGO); the Biogas Technology Research Centre of King Mongkut's University of Technology in Thonburi, Thailand; the Centre for Youth, Family and the Law, a Nigerian NGO; and the Sustainable Ibadan Project, which is part of UN-HABITAT.

This plant, which is one of the largest biogas installations in Africa, was designed to provide gas to 5400 families a month at around a quarter of the cost of liquefied natural gas. The pilot biogas plant started operation in May 2008. The United Nations Development Programme (UNDP) in Nigeria is providing full funding for the biogas plant. The expected rate of return on investment on the plant was 2 years, while it had a useful lifetime of fifteen years. The biogas yield was estimated at 1500 cubic meters of biogas (900 m³ of pure methane) per day based on slaughtering 1000 cows at Bodija Market abattoir on a daily basis. The biogas generated is used for cooking. The sludge from the biogas reactors was transformed into organic fertilizer and sold to the Oyo State Fertilizer Board. The Cows-to-Kilowatts was a 2005 winner of the Supporting Entrepreneurs for Environment & Development (SEED) Awards, which honor outstanding new entrepreneurial ideas for sustainable development worldwide. Other awards include the Global Social Benefit Incubator Program (GSBI), Santa Clara University, California, USA (July, 2006); feature of Cows to Kilowatts at AFRICA LEADS (June, 2006); feature of Cows to Kilowatts in World Economic Forum publication (September, 2007).

Although biogas technology is not common in Nigeria, considerable local capability exists for building both floating dome and fixed dome bio digesters using a variety of bio resources, and the technology has been domesticated with a number of pilot biogas plants built. Examples include a human waste biogas plant at the Zaria prison, cow dung based biogas plants at the Fodder farm of the National Animal Production Research Institute (NAPRI), Zaria and Mayflower Secondary School Ikenne, Ogun State; an 18 m³ capacity pig waste biogas plant at the pig farm of the Ojokoro/Ifelodun Cooperative Agricultural Multipurpose Society in Lagos State. A number of indigenous outfits are producing economically viable systems for converting municipal waste to energy.

Despite the slow uptake of biogas technology in Nigeria, various research work on the science, technology and policy aspects of biogas production has been carried out by researchers in the area of biogas production using different substrates and varying operating parameters. A few mentioned here are, a study carried out on the effects of media material and its quantity on biogas

yield at the University of Agriculture Makurdi and University of Ibadan by Itodo *et al.* (1992); they revealed that there was no definite relationship between the quantity of media material used and biogas yield, but the media material accelerated the commencement of biogas production. Garba and Sambo (1992) studied the effect of operating parameters like temperature, *pH*, nutrient addition, mixing ratio and retention period on the biogas production rate in Sokoto State. They found a temperature range of 30–40°C and 40–60°C led to a higher rate of gas production, a *pH* of 7.0 to be ideal for optimum gas production and that when cow dung and water were combined in the ratio 1.5:1 optimum gas yields were obtained. Eleri (2007) studied the effect of different inocula on biogas production from kitchen waste and found that biogas yield varied with different inocula and that poultry waste as inoculate had the highest biogas yield. Others like Machido *et al.* (1996) and Zuru *et al.* (1997) studied the effect of the addition of inorganic nutrients on the production of biogas from cow dung. Aliyu *et al.* (1996) found that seeding the digester led to an increase in gas production by 27%, in addition to early gas production. Lastly, Maishanu and Maishanu (1998) investigated the influence of inoculum age on biogas production from cow dung and found that the three-week and two-week old inocula gave the highest specific gas production rates, and also the addition of inocula was found to eliminate the initial lag phase in all the digester with inocula.

11.3.1 Technical characteristics of biogas digester

There are three common designs for biogas digesters. *The fixed dome*: consisting of an airtight container constructed of brick, stone or concrete, the top and bottom being hemispherical. Sealing is achieved by building up several layers of mortar on the digester's inner surface. The digester is fed on a semi-continuous basis (usually about once a day) and the gas produced rises to be stored under the upper dome. The typical feedstock for this kind of digester is animal waste, human excreta, and agricultural waste. The retention time here is usually 60 days at 25°C.

The fixed dome Chinese model biogas plant (also called a drumless digester) was experimented on in China as early as the mid-1930s. This model consists of an underground brick masonry (cement mortar) compartment for the digestion chamber with a concrete dome on the top for gas storage and a displacement pit. Thus, in this design the digestion chamber and the gas storage dome are combined as one unit. It uses the 'displacement principle' of operation. Gas is collected at the upper portion of the digester (dome). Slurry in the digester pit is forced up into a slurry reservoir due to the pressure created by the gas collected in the curved structure (dome) of the digester. As the biogas is used from under the concrete dome, the slurry flows back from the reservoir to replace it (Madan *et al.*, 2004).

The advantages of this design include: low initial costs and long useful life-span, no moving or rusting parts involved, the basic design is compact, saves space and is well insulated, and construction creates local employment. The disadvantages are: masonry gasholders require special sealants and high technical skills for gastight construction; gas leaks occur quite frequently; fluctuating gas pressure complicates gas utilization; the amount of gas produced is not immediately visible, plant operation is not readily understandable; fixed dome plants need exact planning of levels; excavation can be difficult and expensive in the bedrock. Fixed dome plants can be recommended only where experienced biogas technicians can supervise construction (GTZ, 1999).

The Floating Cover: this was first designed by India's Khadi and Village Industries Commission (IKVIC) and consists of a cylindrical container, constructed of brick or concrete and reinforced with chicken wire. The digester construction strength is not as critical as with the fixed dome type since the only pressure on the walls is the fermenting material, the gas produced floats upward as the pressure increases. The cover is made of mild steel. The main problem with this design is the cost, corrosion and maintenance of the cover. Typical retention time is 30 days in warm climates and up to 50 days in colder regions. The usual feedstock is cattle manure fed on a semi-continuous basis. With the introduction of the fixed dome Chinese model plant, the floating drum plants became superseded due to comparatively high investment and maintenance cost along with other design weaknesses (GTZ, 1999).

The advantages of this design are: floating-drum plants are easy to understand and operate, they provide gas at a constant pressure, and the stored gas-volume is immediately recognizable by the position of the drum. Gas-tightness is no problem, provided the gasholder is derusted and painted regularly. The disadvantages include: the steel drum is relatively costlier to build, difficult to transport and requires high investment in maintenance cost. Removing rust and painting has to be carried out regularly. The lifetime of the drum is short (up to 15 years; in tropical coastal regions about five years). If fibrous substrates are used, the gasholder shows a tendency to get “stuck” in the resultant floating scum (Shakya and Charushree, 2009a).

The Bag Digester: This type of digester comprises a long cylinder of either polyvinyl chloride (PVC) or a material known as red mud plastic, developed in 1974 from the residue of bauxite smelted in aluminum production plants. Incorporated in the bag are inlet and outlet pipes for the feedstock and slurry and a gas outlet pipe. Gas produced is stored in the bag under a flexible membrane. Typical retention time varies with the substrate being used from 60 days at 15–20°C to 20 days at 30–35°C (ECN, 2005).

11.3.2 Mechanisms of methanogenesis

Methanogenesis simply means generation of methane from organic wastes by microorganisms. It is also known as methane formation, bioconversion, anaerobic digestion, bio methanization or simply methanization (Fig. 11.1; Garba, 1999). To better understand the mechanism of methanogenesis, there is a need to understand the biochemistry of the process and the microorganisms involved in the process. Methanogenesis is known to occur in four stages of hydrolysis, fermentation, acetogenesis and finally methanogenesis.

11.4 POTENTIALS OF BIOGAS TECHNOLOGY FOR SUSTAINABLE DEVELOPMENT

Biogas could grow into an important source of energy for Nigeria. A study, based on an analysis of population growth, household income, government intervention, and availability of waste materials, projects future quantities of household biogas plants to range between 144,350 and 2,165,250 in the period 2000–2030. Biogas offers advantages in soil amelioration, substitution for commercial fertilizer, improved sanitation, reduced use of fuel wood, and a reduction in greenhouse gases. Global experience shows that the use of biogas technology can improve human well-being (improved sanitation, reduced indoor smoke, better lighting, reduced drudgery for women, and employment generation) and the environment (improved water quality, conservation of resources – particularly trees, reduced greenhouse gas emissions) and produce wider macro-economic benefits to the nation (WINROCK, 2007). In Nigeria where 95,000 women and children die annually from indoor air pollution, biogas for cooking has the potential to reduce this number significantly. The rapid deforestation in the southern part of Nigeria and the desertification in the north can be reduced with the introduction of biogas for cooking and heating in households and institutions. Biogas technology has the potential to mitigate a wide spectrum of environmental undesirables: it improves sanitation, it reduces greenhouse gas emissions, it provides a high-quality organic fertilizer, and it reduces demand for wood and charcoal for cooking, preserving forested areas and natural vegetation (Venro, 2009). However, in Nigeria as in other countries in sub-Saharan Africa, biogas's greatest benefit is its potential to alleviate health problems arising from indoor air pollution.

11.5 BARRIERS TO BIOGAS TECHNOLOGY

There are some major constraints to the development and widespread uptake of biogas technology in Nigeria, some of which are cost, livestock raising patterns, lack of awareness and sociocultural beliefs. Though studies have shown household biogas plants to be economically feasible over

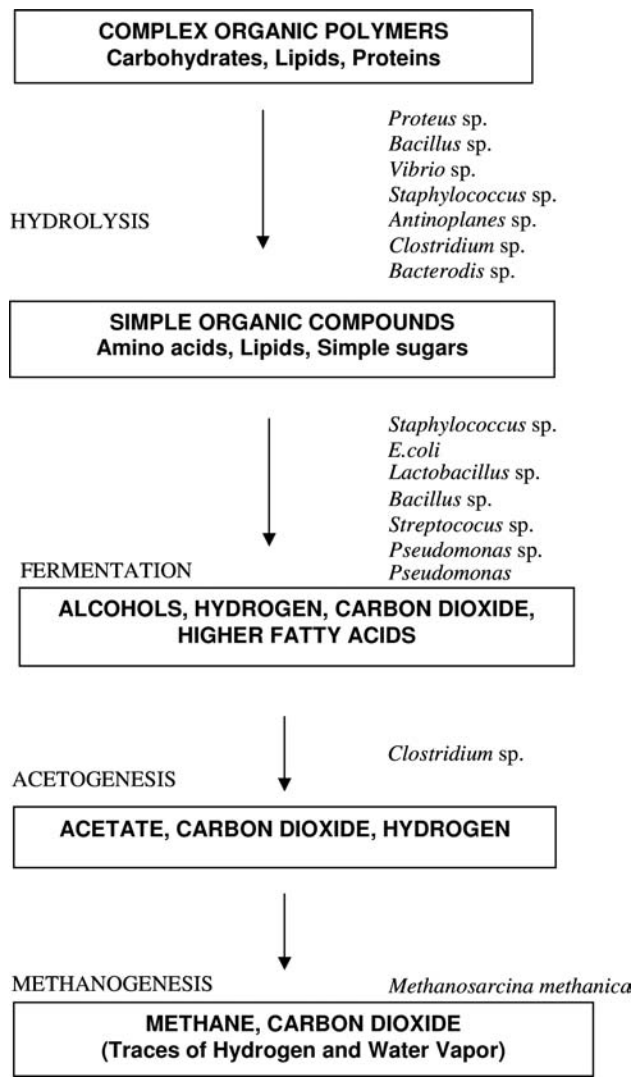


Figure 11.1. Stages of methanogenesis (Garba, 1999).

time, the initial price is high and constitutes a barrier, especially to households. Other constraints to households include the amount of space required for the plant, water supply issues and the availability of enough feedstock to generate sufficient biogas for cooking and/or heating. In most communities in Nigeria, the houses are clustered together and so it might be difficult to find space to install biogas plants for each household. The unavailability of or limited access to water also creates a huge challenge as biogas plants require water in equal proportion to the manure to be used. The livestock-rearing pattern is another major constraint, unlike countries like Nepal, India or China it is not common in Nigeria to find communities where each household has 2–3 cattle that are stabled at home. What is more common is to find livestock such as goats and birds like chicken, turkey or ducks reared in free grazing style at home while livestock like cattle and sheep are reared in a nomadic pattern.

Other challenges to biogas technology development are socio-cultural such as lack of knowledge about biogas, fear and dangers involved in using gas, beliefs that fuel wood imparts a better

flavor to cooked food, and the belief that it is unhygienic to cook with waste matter from humans or animals.

Technical issues such as poor design, lack of training on proper operation and maintenance of plants and in some instances unavailability of materials to repair the biogas plants can also constitute a barrier to rapid development and widespread use of biogas plant. A critical barrier to widespread biogas technology uptake is the absence of a definite and coherent biogas technology development program by the government.

11.6 RECOMMENDATIONS FOR SCALING UP BIOGAS TECHNOLOGY IN NIGERIA

From the experience of biogas technology dissemination in Nigeria and other countries in sub-Saharan Africa, it is obvious that biogas promotion needs to be led by government. However, despite the acknowledged technical viability, advantages and potentials of biogas technology in Nigeria, the government does not have a definite biogas program in place. The huge success recorded by countries such as Nepal, India and China can be attributed in part to the development of a national program led by the governments of those countries. In Nigeria, the Energy Commission of Nigeria can lead such a national program on biogas promotion and dissemination. The Nigerian program would have four main objectives: (i) the provision of sustainable energy, (ii) the reduction of indoor air pollution, (iii) the reduction of desertification and deforestation, and (iv) proper waste disposal. The main focus area for the program would be the commercial and institutional setting. This is because commercial and institutional settings like abattoirs, markets, prisons and schools constitute areas of quick wins in Nigeria due to factors such as availability of funds, availability of feedstock, availability of space and access to water.

Abattoirs are great examples of areas of quick wins in biogas technology development in Nigeria. As the example from the Cows-to-Kilowatt projects shows abattoirs can be a source of energy supply by generating biogas that can be used for cooking, lighting and heating. According to the Cows-to-Kilowatt project case study note, about 1000 cows are slaughtered at the Bodija market abattoir on a daily basis, which would produce 1500 m³ of biogas (900 m³ of pure methane) per day. This, in turn, amounts to 5400 cylinders of cooking gas per month. If used to generate electricity the 1000 cows slaughtered per day, would generate approximately 3600 kWh of electricity per day. Other places that are capable of fast tracking biogas technology development are schools, prisons, markets, hotels and hospitals. This is because these institutions and organizations are already accustomed to spending heavily on traditional biomass in the form of wood fuels for cooking and heating needs. They also have the advantage of availability of funds, space, feedstock (in the form of human waste, sewage and kitchen waste), and access to water and staff that can be trained to operate and maintain the plants.

On the household front, constraints such as costs, lack of space and livestock raising patterns can be addressed in a number of ways:

- The high cost can be addressed by modifying plant design to incorporate locally available materials in the construction of the plant and the biogas produced can be used for income generating purposes in addition to domestic uses.
- On the issue of space, where most households live in close clusters, community biogas plants could be introduced.

11.7 CONCLUSIONS

Biogas technology, though a simple, adaptable and readily usable technology, is not a significant part of the energy sector in Nigeria. Though the potential of biogas technology to improve the energy, health and environmental challenges in Nigeria has been well studied and documented, there is no definite program on biogas in Nigeria.

A look at successful biogas programs in other African and Asian countries has shown that there is an urgent need for the Nigerian government to launch a program on biogas that encourages public–private partnerships in the development of this technology.

The Nigerian government needs to move away from pilot projects demonstrating the technology and develop a program that would stimulate the growth of the biogas sector. A detailed study of the Nepalese biogas program shows that factors that enhanced its success include subsidy and quality control mechanisms, incentives that encourage private companies to produce plants, creating demand for biogas digesters, standardized technology, and an independent program.

The Nigerian program can focus on:

- *Market development*: This can be achieved by creating policies and technical standards to guide and facilitate the development of the biogas industry in Nigeria, integrating biogas technology development into the overall investment policies as well as developing appropriate policy frameworks for investors. The setting of national targets and timelines for reducing indoor air pollution would also spur the creation of new and long-term markets.
- *Financial sector reform*: Literature has identified inadequate finance as a factor limiting biogas technology development in Nigeria and other African countries so there is a need for innovative financial mechanisms to drive the development of biogas technology in Nigeria on a sustainable basis. Strategies that encourage the channeling of funds towards sustainable energy options such as biogas is a right step in the financial reform process. The expansion of options for microfinance and the providing of funds toward small and medium scale enterprises would go a long way in eliminating this barrier.
- *Capacity building*: This is also very important and crucial to the success of this programme. The capacity of the federal government, state government, local government, private sector actors, companies, Non-governmental organizations and civil society organisations levels all need to be strengthened. According to the UNDP (2010), Capacity development goes far beyond traditional notions of capacity building typically defined by ‘training’ and/or ‘management’. A diverse array of functional and technical capacities: (i) planning, oversight, and monitoring; (ii) policies and regulations; (iii) situational analysis; (iv) stakeholder dialogues, communication and community mobilisation; (v) setting up and enhancing institutions; (vi) training of programme implementers and community members; and (vii) implementation and management, must all be developed and put in place.
- *Public–private partnership*: The program should have a clearly defined public–private partnership strategy. The private sector’s ability to bring the much needed capital and the ability to design, construct, operate and maintain biogas plants, coupled with the ability of the public sector to develop long-term, low-risk policies is what makes the partnership effective.

For the Nigerian program to succeed there has to be a strong policy, legislative and regulatory framework that stimulates investment in biogas technology development by special incentives and fair and stable regulations.

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CHAPTER 12

The influence of biodegradability on the anaerobic conversion of biomass into bioenergy

Rodrigo A. Labatut

12.1 INTRODUCTION

Anaerobic digestion has been used to stabilize organic wastes, offset greenhouse gas (GHG) emissions, control odors, promote environmental management of nutrients, and produce clean and local renewable energy. The array of organic substrates subjected to anaerobic digestion today varies widely in both diversity and complexity. Livestock manure, from concentrated animal feeding operations (CAFOs), and waste activated sludge (WAS), from wastewater treatment plants (WWTPs) have been traditionally stabilized in on-site anaerobic digesters. Also, an increasing number of CAFOs co-digest livestock manure with imported, high-strength substrates to increase their energy production, take advantage of tipping fees, and improve the economic viability of the farm operation (Scott *et al.*, 2010). In addition, the organic fraction of municipal solid waste (MSW) is separated in certain municipalities in Europe and treated in anaerobic digesters to reduce biomethane emissions from landfills and produce bioenergy. On the other hand, grasses and cereals are grown in biogas plants in Europe with the main purpose of producing bioenergy in anaerobic digesters (Weiland, 2006).

The overall bioenergy production of any system depends on the operating conditions and the characteristics of the biomass material. Under a particular solids retention time (SRT) and temperature regime, the biomethane yield of the system will be primarily determined by the chemical strength and biodegradability of the substrates. The chemical strength can be defined in terms of the chemical oxygen demand (COD), a parameter that can be determined *via* standard analytical methods or calculated from the chemical composition of the material. The COD defines the energy density of the substrate, and thus, the theoretical biomethane yield of such material. However, the portion of material available for enzymatic and microbial utilization, defined as the biodegradable fraction, will constrain the extent of substrate that can be stabilized and determine the actual, observed biomethane yield. Furthermore, in conventional wet anaerobic digestion only a small portion of the influent substrate volume consists of solid material. Table 12.1 presents the total solids (TS) and volatile solids (VS) content of various substrates, including co-digestion samples containing two or more co-substrate materials. A common biomass, cow manure, is typically composed of 12% dry matter, 10% organic matter, 2% ash, and 88% water, where approximately 50% of the organic matter is biodegradable. Thus, only 5% of the raw substrate (v/v) has the potential of producing biomethane (Fig. 12.1).

Biodegradability is usually assessed *via* long-term batch tests, particularly using the biochemical methane potential (BMP) assay (Owen *et al.*, 1979). The difference between the observed biomethane yields, obtained with the BMP assay, and the theoretical biomethane yields, represent the biodegradable fraction of substrates. To account for the differences in organic matter content of the different materials, the observed biomethane yield is normalized by the mass of substrate volatile solids (VS) subjected to digestion. Figure 12.2 shows the observed and theoretical specific biomethane yields (SMY) and the corresponding equivalent bioenergy yield of the substrates listed in Table 12.1. As observed in the plot, a wide range of SMY exists – with biomass materials producing as low as 100 L CH₄ per kg of VS, to substrates that can potentially produce over six times that, i.e. an overall energy equivalent of 22 MJ/kg VS.

Table 12.1. Total solids (TS) and volatile solids (VS) content of various substrates; numbers represent co-digestion ratios between co-substrates.

Substrate	TS [g/L]	VS [g/L]
Used vegetable oil (VO)	991.0	988.8
Ice cream (IC)	113.8	109.1
Mn50-DF25-IC25	106.9	96.9
Dog food (DF)	132.2	125.6
Cheese whey (CW)	78.7	66.8
Invasive aquatic plants (AP)*	97.7	52.9
Mn75-VO25	263.6	235.4
Potatoes (Pt)	177.4	163.5
Corn silage (CS)	217.3	200.7
Mn75-MP25	148.5	136.9
Cabbage (C)	78.6	72.0
Mn75-CW25	68.5	57.7
Dairy manure (Mn)	124.0	102.1
Mn90-CW10	83.2	68.4
Mn90-MP10	101.9	89.8
Meat pasta (MP)	381.8	340.6
Mn75-SG25	308.0	284.4
Switchgrass (SG)**	930.1	904.9
Corn leachate (CL)	49.2	35.4

*Average of five invasive aquatic plants found in water streams in New York State.
** Air-dried.

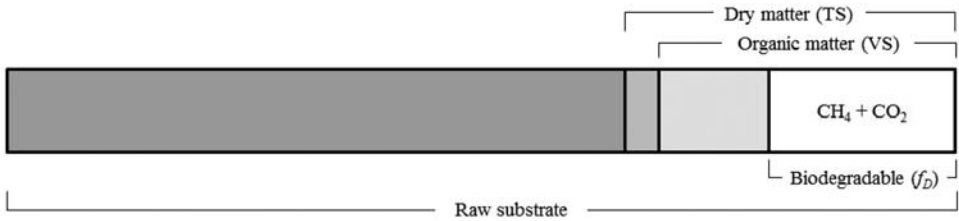


Figure 12.1. Portion of raw substrates with the potential of producing biomethane. The residue is water.

The influence of substrate biodegradability is apparent. High-strength, lipid-rich substrates have the potential of producing high biomethane yields as is high VS content (Table 12.1), but their biodegradability is usually hindered by inhibition resulting from the accumulation of long chain fatty acids produced during the hydrolysis of neutral lipids. Proteins and carbohydrates have comparable but lower energy densities than those from lipids. In addition, biomethane yields from protein-rich materials can be limited by potentially inhibitory digestion products, i.e. ammonia. Sugar-rich substrates, such as whey, a yogurt- or cheese-processing by-product, are fairly biodegradable but highly diluted (see Table 12.1); thereby, their biomethane yields are low per mass of raw material. Lignocellulosic materials have low energy densities and are fairly recalcitrant under anaerobic conditions.

12.2 THEORETICAL ASPECTS AND ASSESSMENT OF SUBSTRATE BIODEGRADABILITY

Substrate biodegradability is primarily characterized in terms of the biodegradable fraction. It represents the maximum extent of substrate biodegradation obtained under batch conditions at a

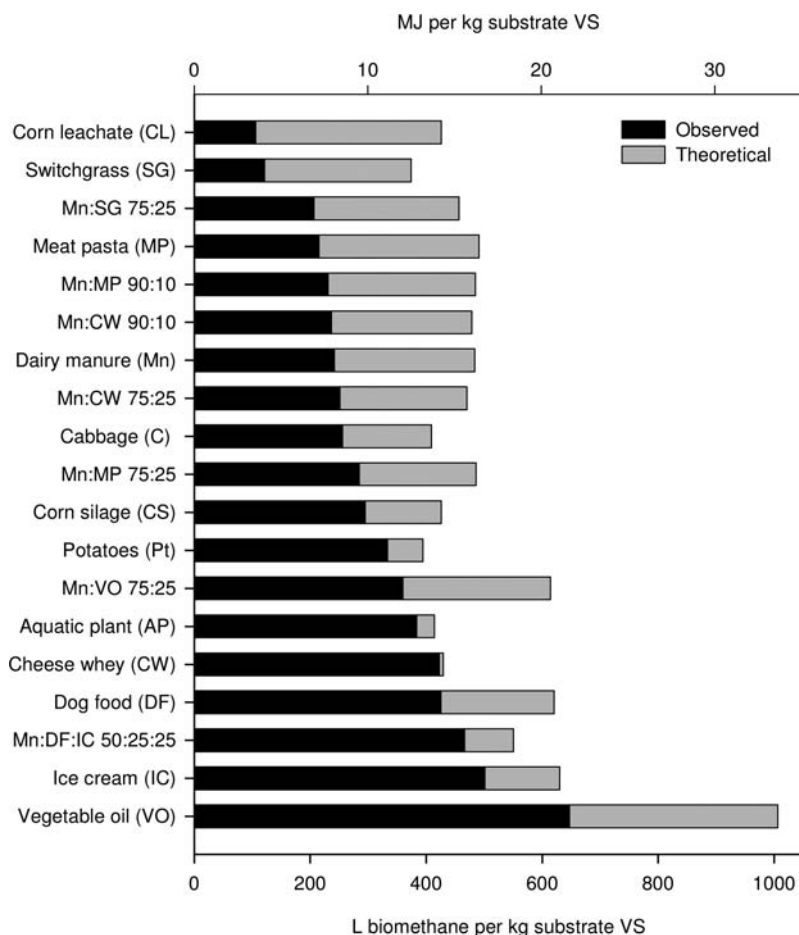


Figure 12.2. Observed (black) and theoretical (grey) specific biomethane and bioenergy yields (0°C and 1 atm) of various substrates (as Table 12.1); observed data from Labatut *et al.* (2011) – obtained at mesophilic conditions (37°C) using the *BMP* assay; values correspond to the average of triplicates, error bars are omitted for clarity; equivalent bioenergy yields calculated assuming the low heating value (*LHV*) of methane, i.e. 33.9 kJ/L ; theoretical yields calculated using the Buswell Formula (see text).

hypothetical incubation time equal to infinity. The biodegradable fraction is, therefore, an ultimate parameter – that is, independent of the rate of biodegradation (Labatut, 2012).

Traditionally, biodegradability and organic matter concentration of wastewater streams has been characterized in terms of the biochemical oxygen demand (*BOD*). However, the *BOD* assay is performed under aerobic conditions, which represents fundamental limitations for characterizing biodegradability of substrates to be treated in anaerobic digesters. Alternatively, the biochemical methane potential (*BMP*) has become the standard method for determining substrate biodegradability under anaerobic conditions. Whereas the *BOD* measures the amount of dissolved oxygen consumed by microorganisms, the *BMP* measures the amount of methane produced by microorganisms. The amount of biodegradable substrate remaining at any given time during the *BMP* assay can be modeled by a first order function, as given by:

$$S = S_0 e^{-kt} \quad (12.1)$$

where S is the amount of substrate remaining at time t [g/L, mol/L], S_o is the total amount of substrate observed at the beginning of incubation [g/L, mol/L], k is the first-order biodegradation (or biomethane production) rate constant [d^{-1}], and t is the time of incubation [d]. When the recalcitrant portion of the substrate, as given by S_r [g/L, mol/L], is accounted for, equation (12.1) becomes:

$$S = S_r + (S_o - S_r)e^{-kt} \quad (12.2)$$

The fraction of substrate stabilized during a *BMP* assay is directly proportional to the biomethane evolved; thus, equation (12.2) can be written as:

$$B = B_u - S_r - B_o e^{-kt} \quad (12.3)$$

where B is the observed specific biomethane yield at time t [L/kg, mol/L], B_u is the theoretical specific biomethane yield [L/kg, mol/L], and B_o is the observed specific biomethane yield at the end of the *BMP* assay [L/kg, mol/L]. Equations (12.2) and (12.3) are plotted in Figure 12.3. As shown, B_o (S_r) is determined at the time the biomethane production (substrate biodegradation) approaches the plateau phase ($k \rightarrow 0$) – which usually occurs within the first 30 to 45 days of the *BMP* assay, mainly depending on the substrate characteristics and the anaerobic thermal range (e.g. mesophilic, thermophilic).

The substrate biodegradable fraction, f_D (decimal), can be determined several ways, depending on the type of data available. The most direct method is to measure the initial (S_o) and final (S_r) substrate concentrations (VS basis) in the batch reactor and determine the fraction of substrate that has been stabilized during digestion:

$$f_D = \frac{S_o - S_r}{S_o} \quad (12.4)$$

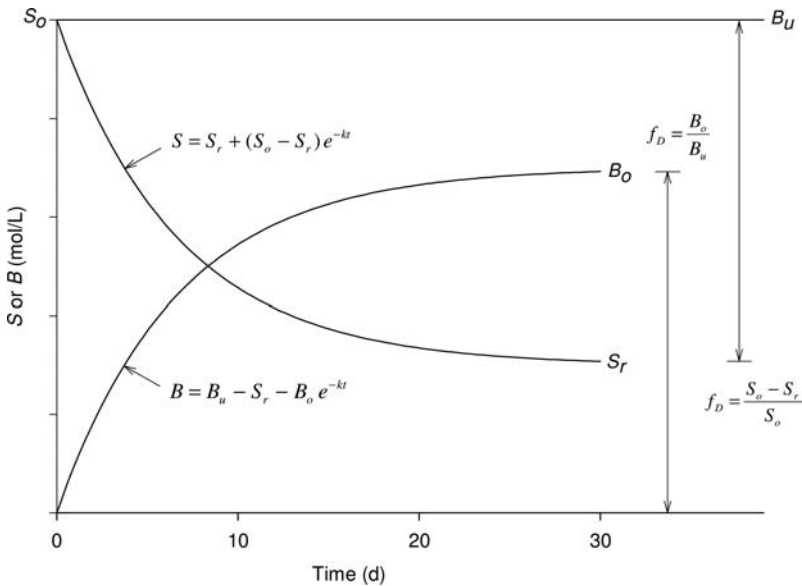
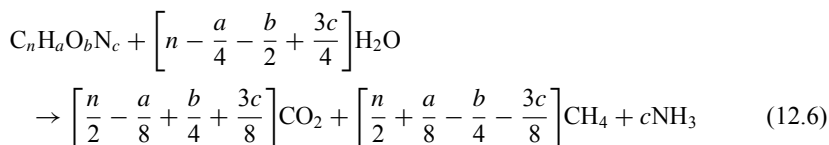


Figure 12.3. Theoretical biomethane yield (B) and substrate biodegradation (S) during the course of a *BMP* assay; obtained using equations (12.2) and (12.3); S_o is the total (initial) substrate added to the *BMP*, S_r is the (recalcitrant) substrate remaining at the end of the *BMP*, B_o is the observed biomethane yield at the end of the *BMP*, B_u is the theoretical (ultimate) biomethane yield of the substrate (calculated from its chemical composition); f_D is the substrate biodegradable fraction.

Alternatively, when the chemical composition of the substrate is known, f_D can be calculated from the ratio of observed to theoretical specific biomethane yields (SMY):

$$f_D = \frac{B_o}{B_u} \quad (12.5)$$

The theoretical SMY (B_u) of a generic substrate (i.e. $C_nH_aO_bN_c$) can be derived from the stoichiometric formula developed by Symons and Buswell (1933):



Lastly, when chemical oxygen demand (COD) data are available, f_D can be obtained by the ratio of biodegradable to total COD:

$$f_D = \frac{COD_D}{COD_T} \quad (12.7)$$

where COD_D is the biodegradable chemical oxygen demand [g/L], and COD_T is the total chemical oxygen demand [g/L]. COD_D can be calculated from the theoretical 350 L of biomethane yielded (at STP) per kg of COD stabilized (McCarty, 1964), and using B_o as obtained from the BMP assay. COD_T can be determined analytically (APHA, 1995), or theoretically, from the chemical composition of the substrate and the stoichiometry of oxidation-reduction reactions.

12.3 FACTORS LIMITING SUBSTRATE BIODEGRADABILITY

Most organic substrates are made up of a mixture of carbohydrates, proteins, and lipids. During anaerobic digestion, these composite materials undergo a series of chemical transformations, where methane and carbon dioxide are the main gas products (Fig. 12.4). In the first step, the organic/biodegradable fraction of polymers is hydrolyzed to soluble products *via* extracellular enzymes that allow their passage across the cell membrane. Once in the cell, sugars, amino acids, and long-chain fatty acids are fermented (or oxidized, in the latter case) to volatile fatty acids, alcohols, carbon dioxide, hydrogen, as well as nitrogenous and sulfurous compounds. With the exception of acetate, volatile fatty acids are converted to additional acetate, hydrogen, and carbon dioxide. In the final step, methane is produced *via* either cleavage of acetate or reduction of carbon dioxide with hydrogen.

Influent substrate characteristics influence the microbial groups involved in the processes, the biochemical conversion pathways, and the thermodynamic balance and kinetics of the biochemical reactions. In particular, the stoichiometry of the reactions, and thus the ultimate biodegradability of the influent material, is determined by the physical properties and chemical composition of the composite substrates and its impact on *microbial bioenergetics*, *polymer complexity*, and *metabolic inhibition*.

12.3.1 Bioenergetics: cell synthesis vs. metabolic energy

Heterotrophs consume organic matter both for metabolic energy and for cell synthesis. While most of the electrons derived from substrate biodegradation are used towards the production of energy, a small percent is reserved for the synthesis of new cell material. The fractions of electrons going to energy and synthesis depend largely upon the type of substrate being degraded and the digester SRT. Using the equations developed by McCarty (1972) based on the stoichiometry and free energies of microbiologically-mediated reactions, it is possible to estimate the microbial cell

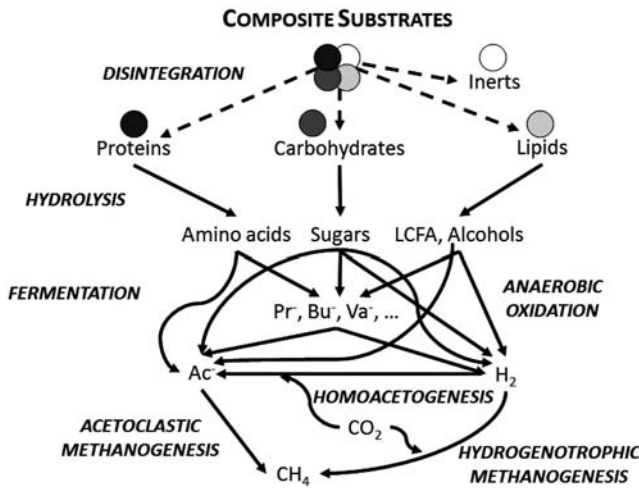


Figure 12.4. Major bioconversion pathways involved in the anaerobic digestion of complex substrates; LCFA: long-chain fatty acids, Ac: acetate, Pr: propionate, Bu: butyrate, Va: valerate; adapted from McCarty and Smith (1986), Pavlostathis and Giraldo-Gomez (1991), and Batstone *et al.* (2002).

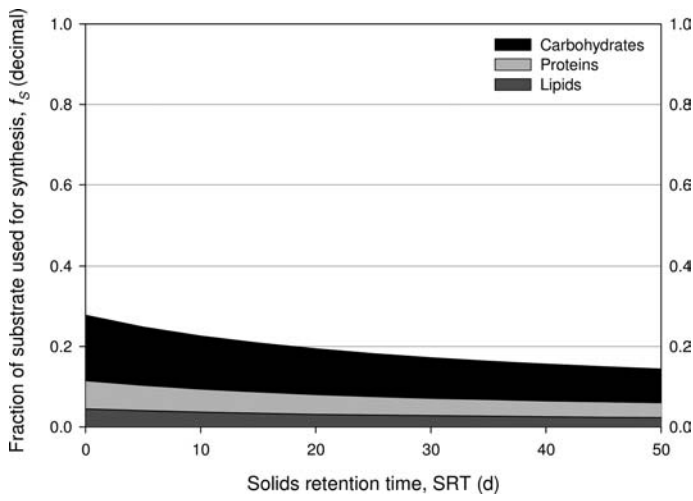


Figure 12.5. Fractions of substrate electrons going to metabolic energy and synthesis for the anaerobic biodegradation of three major biomolecules as a function of the solids retention time (SRT); based on a cell decay rate of 0.03 day^{-1} and using ammonia as nitrogen source (from Labatut, 2012).

yields and the fractions of electron donor used for metabolic energy (f_e) and microbial synthesis (f_s) as a function of the system retention time (Fig. 12.5).

Figure 12.5 demonstrates that regardless of the biopolymer, the longer the SRT, the higher the fraction of substrate going to energy and the lower the microbial yield. It also demonstrates that under any practical SRT, no substrate can be fully converted into energy. Furthermore, the microbial yields obtained from carbohydrates are significantly higher than those obtained from

proteins ($2\times$) and lipids ($6\times$). Indeed, a larger fraction of electrons will be allocated for biomass synthesis in carbohydrate-rich substrates, which will effectively lower the biodegradable fraction of carbohydrates by 17% in a typical design SRT of 30 days. In contrast, the biodegradable fraction of proteins and lipids will be decreased by 7% and 3%, respectively, due to microbial synthesis.

12.3.2 Polymer complexity

Substrates in anaerobic digesters can be found in a variety of forms, from simple monomers, such as sugars and amino acids, to complex associations of insoluble long-chain biopolymers, such as lignocelluloses and keratins. In general, the more complex the influent material is, the slower its biodegradation is, and the more resistant to digestion it is. The degree of complexity is given by the structural and conformational characteristics of the biomolecules composing the substrate. Complex substrates represent a greater limitation to bioconversion because of the increased bimolecular associations and decreased surface area available. Precisely, in the absence of inhibition, biodegradability of complex organic substrates is primarily limited by the physicochemical characteristics of the material and their effect on the extent of bioconversion (e.g. hydrolysis, oxidation, fermentation). Substrates can be classified in three major groups: carbohydrates, proteins, and lipids – the main physicochemical characteristics affecting their biodegradability are described below.

12.3.2.1 Carbohydrates

This group encompasses a diverse array of biomolecules, from readily degradable sugars, to lignin-bound biofibers. Among the factors that determine the biodegradability of carbohydrates are the nature of their glycosidic linkage, inter-molecular forces and linkage between chains, molecular size, and the affinity for the medium (van Soest, 1982). Based on their function in plant cells, biopolymers of carbohydrates (i.e. polysaccharides) can be classified as *structural* and *non-structural*.

Structural carbohydrates, such as lignin-associated cellulose and hemicelluloses (i.e. lignocelluloses) are probably the most common materials found in anaerobic digesters; applications range from animal waste (e.g. cattle, swine, chicken) stabilization to bioenergy production, using agricultural residues (e.g. corn stover) or energy crops (e.g. switchgrass, short rotation woody crops). Furthermore, cellulose constitutes the major organic component of municipal solid waste (Stinson and Ham, 1995).

The lignocellulose matrix is primarily made up of three biopolymers, i.e. cellulose, hemicellulose, and lignin, which are strongly intermeshed and chemically bonded together by non-covalent forces and by covalent cross-linkages (Perez *et al.*, 2002). Cellulose and hemicellulose together make up of 63–78% of the fiber lignocellulose structure, while lignin makes up 15–38% (Angelidaki and Ahring, 2000). In addition, the lignocellulosic matrix includes other biopolymers, primarily pectin and proteins, which add additional complexity and thus resistance to its degradation (Leschine, 1995).

Cellulose is an unbranched polymer, insoluble in water, which consists of several thousands of D-glucose units joined by β -1,4-glycosidic linkages. Hydrolysis of cellulose produces D-cellobiose (β -1,4-bond) which, upon complete hydrolysis, D-glucose is released (Colberg, 1988). Cellulose molecules are strongly associated through inter- and intra-molecular hydrogen-bonding and van der Waals forces that result in the formation of micro fibrils, which in turn form biofibers (Leschine, 1995). Micro fibrils form highly ordered crystalline domains interspersed by more disordered, amorphous regions; the amorphous component is digested more easily by enzymes than the crystalline component (Dale *et al.*, 2005). Figure 12.6 shows the biodegradability fraction of three carbohydrate polymers determined at mesophilic conditions. As expected, the biodegradable fraction of any of the tested carbohydrates, including sugars (data not shown, see Labatut, 2012) is lower than 90% due to the bioenergetics constraints, as discussed in the previous section. Although cellulose appears to be fairly biodegradable under anaerobic conditions (Fig. 12.7), pure cellulose is rare in nature – all structural celluloses are combined to some degree

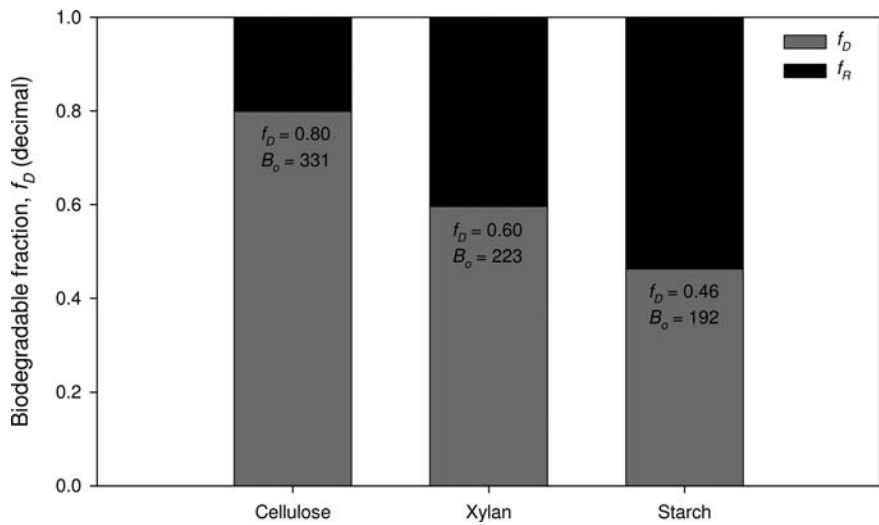


Figure 12.6. Biodegradable fraction (f_D) of three carbohydrate polymers at mesophilic conditions; the grey area corresponds to f_D of the carbohydrate while the black area represents its recalcitrant (f_R), or non-biodegradable, fraction; f_D values shown inside the bars were calculated using equation (12.5), while corresponding observed SMY (B_o), with units of L CH₄ per kg VS (at 0°C and 1 atm), were obtained from *BMP* (data Labatut, 2012); error bars are omitted for clarity.

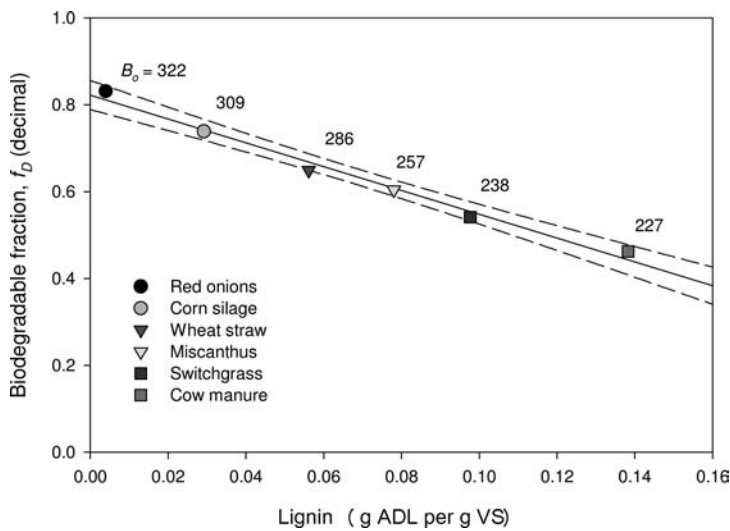


Figure 12.7. Correlation between the acid detergent lignin (ADL) content of six different lignocellulosic materials and the biodegradable fraction (f_D) at mesophilic conditions ($R^2 = 0.99$); the solid line represents the line of perfect fit, and segmented lines set the limits of the confidence intervals at a 95% level; the numbers over the data points denote the observed SMY (B_o), with units of L CH₄ per kg VS (at 0°C and 1 atm), of the corresponding substrates; data from Labatut (2012).

with lignin, hemicellulose, cutin and minerals in the plant cell wall structure (van Soest, 1982). In fact, the biodegradability of cellulose varies from total indigestibility to complete digestibility, depending largely upon the degree of lignification (van Soest, 1982).

Hemicelluloses have a complex carbohydrate structure that consists of different polymers, such as pentoses (e.g. xylose and arabinose), hexoses (e.g. mannose, glucose and galactose), and sugar acids. The dominant component of hemicelluloses is xylan, which primarily comes from agricultural plants, such as grasses and straw (Hendriks and Zeeman, 2009). Xylans have a β -1,4-linked xylopyranose backbone with attached side groups of acetate, arabinofuranose, and O-methyl glucuronic acid (Leschine, 1995). Considering that hemicelluloses surround the cellulose microfibrils and occupy spaces between fibrils, this biopolymer must be degraded, at least partially, before cellulose can be effectively degraded by cellulolytic bacteria (Leschine, 1995). Hemicelluloses have a lower molecular weight than cellulose, and branches with short lateral chains that consist of different sugars, which are easily hydrolysable polymers (Hendriks and Zeeman, 2009). However, the author's data suggest that at least xylan is only partially biodegradable at mesophilic conditions (Fig. 12.7).

Lignin is a highly branched, hydrophobic polyphenolic aromatic compound, primarily located in the cell walls of vascular plants (Colberg, 1988; Hendriks and Zeeman, 2009). Lignin provides rigidity to plant cell walls and resistance to biodegradation, and constitutes the most significant factor limiting biodegradability of lignocellulose in anaerobic digestion systems (van Soest, 1982). Lignin is tightly associated to hemicellulose, which covers cellulose and creates a physical barrier for hydrolytic enzymes (Angelidaki and Ahring, 2000). In fact, biodegradability of hemicellulose is directly related to that of cellulose and inversely related to lignification (van Soest, 1982). To date, only a few studies have assessed the influence of lignin on the extent of biodegradability of lignocellulosic materials (Chandler *et al.*, 1980; Hashimoto *et al.*, 1981; Jung *et al.*, 1997). However, there seems to be a consensus that extent of biodegradability of lignocellulosic materials is related to the lignin content. Indeed, there is a negative relationship between the lignin content and the biodegradable fraction (f_D) in lignocellulosic substrates, as shown in Figure 12.7 – that is, the higher the lignin content, the lower the f_D (and the biomethane/energy production). Lignin in itself is believed to be recalcitrant in anaerobic environments (Zeikus, 1980); however, studies have shown that degradation of lignin is possible under anaerobic conditions (Colberg, 1988; Labatut, 2012; Symons and Buswell, 1933), and particularly by rumen microorganisms (Hu *et al.*, 2008).

Non-structural carbohydrates, such as sugars (monosaccharides, disaccharides) and starches (polysaccharides) are ubiquitous in anaerobic digesters. They usually compose primary municipal wastes and food processing wastes. Most common monosaccharides occur as cyclic (ring) structures of five or more carbon atoms, which are soluble in water and already hydrolyzed. Six-carbon monosaccharides (i.e. D-glucose, D-fructose) are the most common sugars in nature; disaccharides, such as maltose, lactose, and sucrose, consist of two monosaccharides joined covalently by an O-glycosidic bond, which is readily hydrolysable. Sugars, in general, are completely biodegradable under anaerobic conditions. Starch consists of two primary biopolymers, i.e. amylose, which is a linear chain of α -1,4-linked D-glucose units, and amylopectin, which is chain of α -1,4-linked D-glucose with branches of α -1,6-linked D-glucose (Kaplan, 1998). Starch, which is partially soluble in water, is the primary polysaccharide for storing energy in higher plants (Shogren, 1998; van Soest, 1982). Some forms of starches are insoluble and resistant to hydrolysis (e.g. wheat breads), while others are only partially bioavailable (e.g. raw potatoes, banana) (van Soest, 1982). Corn-based starch appears to be incompletely biodegradable, as shown in Figure 12.7.

12.3.2.2 Proteins

In complex substrates subjected to anaerobic digestion, proteins are mainly found as a constituent of either foods (e.g. urban solid wastes, food processing wastes) or active/dead biomass (e.g. waste activated sludge and animal manure). Proteins are natural polymers composed of amino acid units linked covalently one to another through peptide (or amide) bonds, which are formed

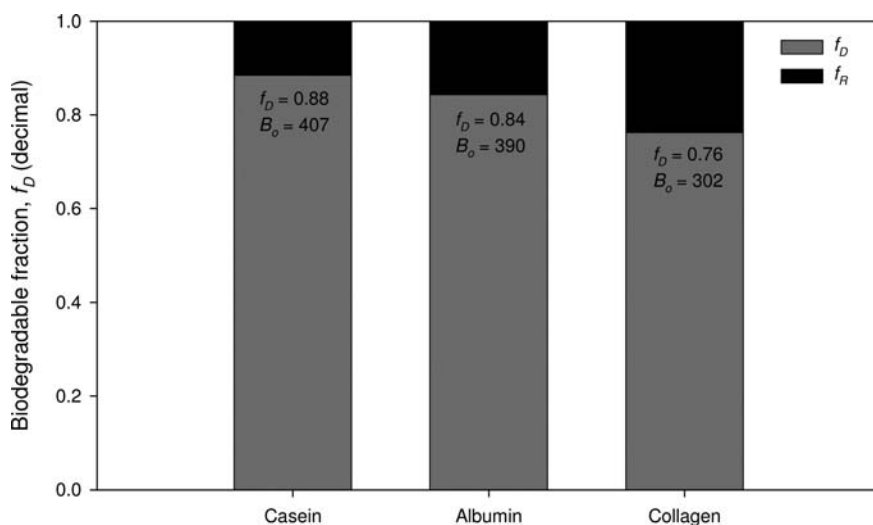


Figure 12.8. Biodegradable fraction (f_D) of three protein polymers at mesophilic conditions; the grey area corresponds to f_D of the protein while the black area represents its recalcitrant (f_R), or non-biodegradable, fraction; f_D values shown inside the bars were calculated using equation (12.5), while corresponding observed SMY (B_o), with units of L CH₄ per kg VS (at 0°C and 1 atm), were obtained from BMP (data Labatut, 2012); error bars are omitted for clarity.

after dehydration of the α -carboxyl group of one amino acid and the α -amino group of another (Nelson *et al.*, 2008). The protein chemical structure is one of the main factors determining the extent of hydrolysis, and thereby its biodegradability. Figure 12.8 shows the biodegradability fraction of three protein polymers of different physicochemical characteristics determined at mesophilic conditions.

There are two major groups of proteins based on their chemical structure: globular proteins, with polypeptide chains folded into a spherical or globular shape, and fibrous proteins, with polypeptide chains arranged in long strands or sheets. Globular proteins, such as casein and albumin, are functional proteins, which are usually readily hydrolysable (McInerney, 1988), and therefore fairly biodegradable as shown in Figure 12.8. In contrast, fibrous proteins, such as keratin and collagen, are structural, insoluble proteins, which are more difficult to hydrolyze (Batstone, 2000), and thus less biodegradable (Fig. 12.8). Proteins are hydrolyzed by extracellular enzymes into their constituent polypeptides and amino acids. Protein hydrolysis in anaerobic environments has not been well studied except for regions in the gut of animals, such as in the rumen (McInerney, 1988). There seems to be major differences between protein degradation in the rumen and in anaerobic digesters. For instance, in the rumen, carbohydrate-fermenting bacteria degrade proteins and the fermentation of amino acids alone does not provide sufficient energy for growth. In anaerobic reactors, however, proteolytic bacteria predominantly mediate protein degradation and the processes involved are energy yielding (McInerney, 1988).

12.3.2.3 Lipids

Lipids are commonly found in wastewater treatment plants as a mixture of fats, oil and grease (FOG). FOG normally accounts for about 30% of the volatile solids in raw wastewater sludge; however, over 50% of the COD reduction and biomethane production during anaerobic digestion comes from FOG degradation (Novak and Carlson, 1970). The simplest lipids are triglycerides, or neutral lipids, which are composed of three fatty acids each in ester linkage with a single glycerol

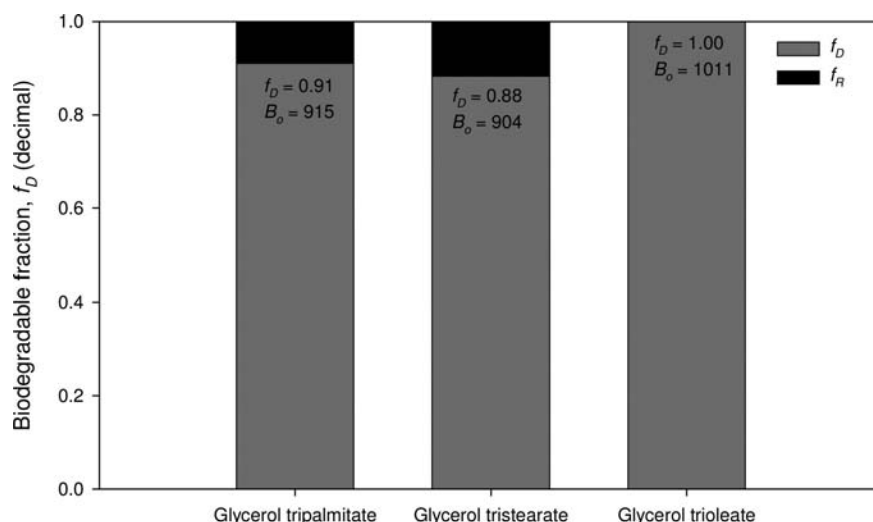


Figure 12.9. Biodegradable fraction (f_D) of three triglycerides at mesophilic conditions; the grey area corresponds to f_D of the lipid while the black area represents its recalcitrant (f_R), or non-biodegradable, fraction; f_D values shown inside the bars were calculated using equation (12.5), while corresponding observed SMY (B_o), with units of L CH₄ per kg VS (at 0°C and 1 atm), were obtained from BMP (data Labatut, 2012); error bars are omitted for clarity.

(Nelson *et al.*, 2008). Triglycerides contribute to waste solids from food processing industries and can comprise up to 65% (w/w) of meat industry wastes (Broughton *et al.*, 1998). Triglycerides are differentiated by its fatty acid chain length, degree of chemical saturation (number of double bonds), and thereby their physical state, i.e. liquid (unsaturated), solid (saturated). Some of the most abundant triglycerides found in wastewaters are saturated 16-carbon glycerol tripalmitate (GTP), saturated 18-carbon glycerol tristearate (GTS), and monounsaturated 18-carbon glycerol trioleate (GTO) (Hatamoto *et al.*, 2007; Miron *et al.*, 2000; Novak and Carlson, 1970). The biodegradability fraction of these triglycerides determined at mesophilic conditions is shown in Figure 12.9. Hydrolysis rates of lipids depend on the aforementioned chemical characteristics as well as their specific surface area (Martinelle and Hult, 1994). The longer the fatty acyl chain and the fewer the number of double bonds, the slower the rate of biodegradation (Novak and Carlson, 1970). However, provided retention times are long enough and concentrations are maintained below inhibitory levels, most lipids are fairly biodegradable, as shown in Figure 12.9. This also agrees with the lower bioenergetics requirements from lipids discussed above.

Triglycerides are hydrolyzed to glycerol and long-chain fatty acids (LCFA) by a group of esterases, called lipases (Pavlostathis and Giraldo-Gomez, 1991). Glycerol is fermented to a variety of volatile fatty acids (VFA), alcohols and formic acid (Broughton *et al.*, 1998). LCFA are primarily degraded *via* α -oxidation (Jeris and McCarty, 1965) by H₂-producing acetogenic bacteria (Bryant, 1979) to acetate and hydrogen (Hanaki *et al.*, 1981), while methanogens consume acetate, formate and hydrogen to produce methane. Accumulation of LCFA can create inhibition of the anaerobic process (Ahring and Nielsen, 2006; Angelidaki and Ahring, 1992; Lalman and Bagley, 2000; Lalman and Bagley, 2001), which can effectively limit the extent of substrate biodegradation. Finally hydrolysis, and thus biodegradability, of fat-rich wastes in anaerobic digesters can also be affected by the floating properties of lipids, which can result in cell biomass washout. Furthermore, the low surface area to volume ratios of these floating aggregates can also decrease their extent of hydrolysis (Gujer and Zehnder, 1983).

12.3.3 Inhibition of biochemical reactions

Under ideal steady-state conditions, the formation and consumption of chemical products as shown in Figure 12.4 proceed until all the bioavailable electrons reach the terminal electron acceptors. However, because different constituents of the substrate degrade at different rates, transient accumulation of intermediate products is expected to occur. Depending on the chemical product, if accumulation persists, biochemical reactions can be inhibited and slow down to the point where they can eventually stop. This process usually occurs when the concentration of certain substances (including *pH*) reaches a level that either disrupts the homeostatic equilibrium of organisms, or imposes thermodynamic constraints for subsequent biochemical reactions. Inhibition commonly arises in secondary digestion stages (e.g. fermentation, β -oxidation, methanogenesis), and can effectively limit the extent of substrate biodegradation. The ability of the digester to withstand transient accumulation of intermediates without causing process perturbation depends on several factors – i.e., the type of constituents composing the substrate mixture, their proportion and concentration in the influent, and the loading rate of the digester. Furthermore, system configuration, operating temperature, and stability of operating parameters, are also key factors in maintaining maximum and stable system performance.

There are several substrates capable of producing intermediate products with the potential to cause process inhibition and instability. Urea- and protein-rich substrates, such as animal manures and industrial wastes, are an excellent source of nitrogen and alkalinity, but can also create high levels of ammonia in anaerobic digesters. Total ammonia ($\text{NH}_3 + \text{NH}_4^+$) and particularly its un-ionized form, are inhibitory to methanogens, by diffusing into the cell and causing proton imbalance (Angelidaki and Ahring, 1993; Kayhanian, 1994; Koster and Lettinga, 1988). Furthermore, most studies conclude that the inhibitory effect of ammonia increases with temperature, with thermophilic organisms being more susceptible than mesophiles (Angelidaki and Ahring, 1994; Chen *et al.*, 2008; Hansen *et al.*, 1998).

The biochemical conversion of simple carbohydrates, such as sugar-rich substrates does not produce highly inhibitory substances; however, their high biodegradability can produce shock loads of volatile fatty acids and associated *pH* drops. On the other hand, lignin-bound carbohydrates are composed of potentially inhibitory substances, such as furfural and phenolic compounds; however, unless raw materials are subjected to some degree of pretreatment, these substances are released slowly enough to not create inhibition.

The anaerobic digestion of fats and oil-containing wastes is maybe the foremost example of inhibition. In this case, anaerobic digestion is hampered due to the inhibitory effect of long-chain fatty acids, which are the major intermediate products of lipid degradation. Figure 12.10 shows the *BMP* curves of three different concentrations of a mixture of triglycerides where inhibition is seen as a slower biomethane production rate at the highest concentration. Although the cause of inhibition from long-chain fatty acids has not been well-established, hypotheses point to physicochemical causes, where the surface-active fatty acids adhere to the organisms' cell wall and impede the passage of nutrients (Henderson, 1973; Rinzema *et al.*, 1994). Similarly, long-chain fatty acids inhibition has been shown to be more pronounced under thermophilic temperatures as compared to mesophilic (Hwu and Lettinga, 1997). Long-chain fatty acids usually accumulate in anaerobic digesters when molecular hydrogen, a major product of their oxidation, reaches thermodynamically limiting levels for the hydrogen-producing organisms to be able to function. Furthermore, the degradation of propionate, a major intermediate of anaerobic digestion of complex substrates depends on even lower partial pressures of hydrogen, accumulates as well (McCarty and Smith, 1986; Schmidt and Ahring, 1993). As with LCFA, higher accumulation of propionate and resulting inhibition has been related to increasing temperatures (Kim *et al.*, 2002; Speece *et al.*, 2006; Wilson *et al.*, 2008).

In addition, nutrient deficiency produces a similar effect to inhibition; certain biochemical reactions can stop altogether due to the exhaustion (or absence) of essential elements/nutrients. Particularly during the long-term digestion of certain substrates, the addition of external nutrients and/or alkalinity may be needed. For example, Agler *et al.* (2008) found that cobalt supplement

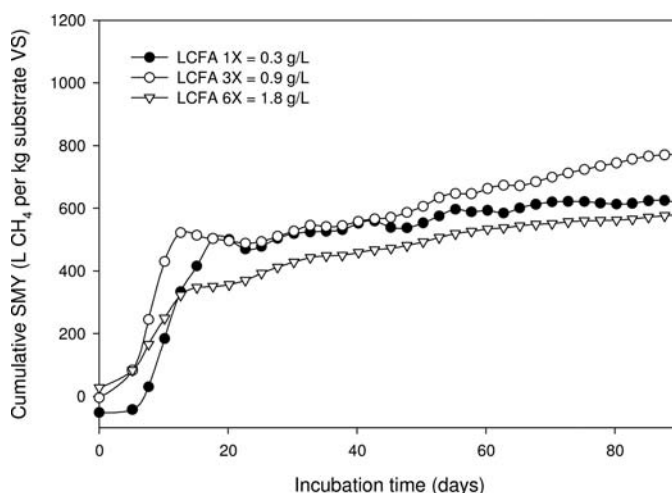


Figure 12.10. *BMP curves showing the specific biomethane yields (at 0°C and 1 atm) of a balanced mixture of long-chain fatty acids (LCFA), i.e. glycerol tripalmitate, glycerol tristearate, and glycerol trioleate at three initial sample concentrations at mesophilic conditions (from Labatut, 2012).*

was required for successful anaerobic digestion of thin stillage (a major by-product of the dry-mill corn grain-to-ethanol process) under thermophilic conditions.

12.4 BIODEGRADABILITY OF COMPLEX, PARTICULATE INFLUENTS: CO-DIGESTION STUDIES

12.4.1 The effect of substrate composition on f_D and B_0 : BMP studies

As discussed above, biodegradability is primarily determined by the physical properties and chemical composition of the influent material. Co-digestion systems probably represent the most complex influent scenario. In this type of operation, the influent is made up of two or more co-substrates (of usually different characteristics) mixed together at specific ratios. Labatut (2012) evaluated the co-digestion of cow manure slurry and dry dog food at varying ratios using the *BMP* assay to investigate the influence of the substrate's physicochemical composition on its biodegradable fraction and biomethane potential (Fig. 12.11). Dog food pellets were used in the study to emulate the multi-component chemical composition of a generic biomass material.

Results showed a linear increase of specific biomethane yields with decreasing manure-to-dog food ratios ($R = 0.99$). This was expected, not only because dog food has a higher B_u , but also because its chemical components were significantly more degradable than those of dairy manure (see Labatut, 2012). The influence of f_D on the biomethane potential becomes apparent when B_u and B_0 are compared for 100% manure and 100% dog food. The difference between the B_u of these pure substrates was only about 100 L CH₄ per kg VS, but nearly 400 between the B_0 , indicating that the difference in biomethane potential of both substrates was primarily due to their difference in biodegradability. Based on the data, the calculated f_D was 0.46 for cow manure and 0.94 for dog food. Thus, dog food was almost completely biodegradable and twice as much as cow manure. Furthermore, the linear increase of B_0 with the decrease of cow manure to dog food ratio suggests that no synergistic or antagonistic effects took place as a result of this co-digestion mixture. Synergistic co-digestion mixtures would observe higher biomethane yields than the sum of the biomethane yields of the weighted individual contributions produced by the pure digestion of manure and dog food. Similarly, antagonism would reflect a lower biomethane yield in the

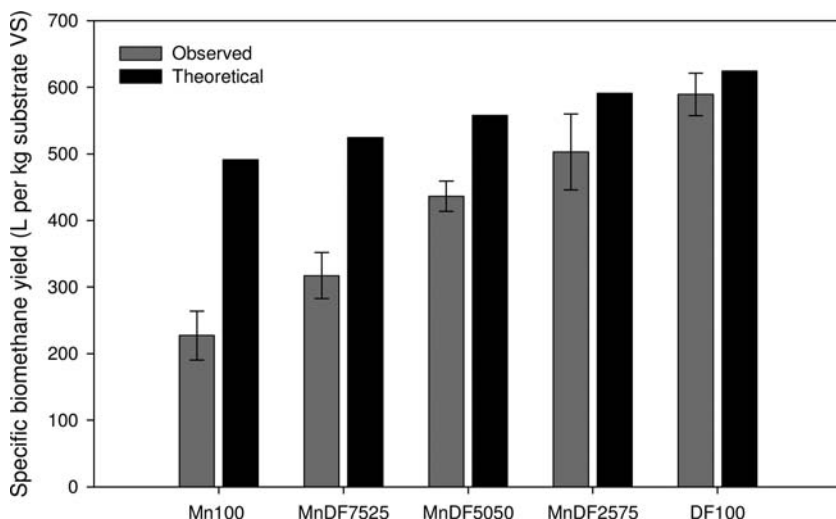


Figure 12.11. Observed SMY (B_o) at mesophilic conditions (at 0°C and 1 atm) for co-digestion samples. Mn = manure, DF = dog food, numbers represent the respective percent contribution to the co-digestion mixture; co-digestion ratios are in a volatile solid (VS) basis; black bars represent the theoretical SMY (B_u) calculated using the Buswell Formula; error bars represent the standard deviation of the replicates; data from Labatut (2012).

co-digestion mixture as compared to the weighted biomethane yield of that mixture. This contrasted with previous studies conducted by Labatut *et al.* (2011) which showed evidence of synergism in selected co-digestion mixtures.

12.4.2 Implications of influent biodegradability on anaerobic digestion systems

As opposed to batch-fed systems, such as the *BMP* assay, substrates in anaerobic digesters are loaded either continuously or semi-continuously (i.e. pulses). Commercial-scale AD systems, such as those treating waste activated sludge (WAS) in wastewater treatment plants (WWTPs) are usually fed continuously, because of the steady nature of the influent flow; however, on-farm AD systems are loaded in pulses, usually every hour for a variable amount of time, depending on the production of manure. For a given reactor design and temperature regime, the biomethane yields of an anaerobic digester will depend on the system's operating conditions, i.e. organic loading rate (*OLR*) and solids or hydraulic retention time (*SRT/HRT*), the influent substrate characteristics, i.e. *COD* and *VS*, and ultimately, the extent of stabilization achieved during the digestion process. The extent (or fraction) of substrate stabilization (or destruction) is given by the difference between the influent and the effluent organic matter concentration, usually measured in terms of *VS* or *COD*:

$$f_s = \frac{S_{inf} - S_{eff}}{S_{inf}} \quad (12.8)$$

where f_s is the extent of substrate stabilization achieved in the anaerobic digester, and S_{inf} and S_{eff} are its influent and effluent *VS* (or *COD*) concentrations [g/L], respectively. Under constant operating conditions, f_s will strongly depend on the biodegradable fraction (f_D) of the influent substrate's different constituents. f_s is normally lower than f_D , because the latter is an ultimate parameter determined over a long period of time, under batch conditions, when substrate biodegradation has essentially stopped. Furthermore, since biodegradation kinetics of anaerobic digesters and batch systems are intrinsically different, the *SRT/HRT* of anaerobic digesters and incubation time of batch systems are not directly comparable (Labatut *et al.*, 2011).

Table 12.2. Summary of the operating conditions for each CSAD during the four periods (P) evaluated in Labatut (2012).

Period (P)	Days	HRT [d]	Composition [% VS basis]	
			Cow manure	Dog food
Start-up	0–62	30	100, 50, 25%	Balance
P-1	63–330	20	25%	Balance
P-2	331–360	15	25%	Balance
P-3	361–498	15	75%	Balance
P-4	499–544	10	75%	Balance

The influence of biodegradability on the performance of semi-continuously-fed anaerobic digesters was evaluated by Labatut (2012). In the study, continuously-stirred anaerobic digesters (CSAD) were used to co-digest cow manure slurry and dry dog food at mesophilic and thermophilic conditions. In this review, we present the results obtained at mesophilic conditions, to direct the attention mainly on the effects of biodegradability, rather than temperature regime, on the system's performance (see Labatut, 2012). Two different cow manure-to-dog food ratios, i.e. 25:75 and 75:25, respectively (VS basis), and three different *HRT* were evaluated during 544 days, which resulted in a total of four distinct operating periods, as detailed in Table 12.2.

The compositional characteristics of these two co-digestion influents as well as the biogas/biomethane production rates, specific biomethane yields (*SMY*), and efficiency of volatile solids stabilization (f_s) at each operating period, are shown in Figure 12.12. The difference in composition between the two influent co-digestion ratios is apparent. The 25:75 manure-to-dog food ratio creates a well-balanced proportion between proteins, lipids, non-structural carbohydrates, and lignocellulosic carbohydrates. At a 75:25 manure-to-dog food ratio, the amount of lignocellulosic material is almost half of the influent substrate. Details of the compositional studies can be found in Labatut (2012).

As expected, the operating periods (P-1, P-2) with the influent co-digestion mixture with the higher amount of manure, i.e. 75:25, present lower observed specific biomethane yields (*SMY*) and volatile solid stabilization than the operating periods (P-3, P-4) with the influent with the higher proportion of dog food, i.e. 25:75. Composition of dog food is mostly made up of easily biodegradable components, whereas cow manure is mostly composed of lignocelluloses, which constituted over 56% of the organic matter (VS) Labatut (2012). However, despite the lower biodegradability of the influent composition at P-4, biogas/biomethane production rates were higher than at P-1, as the organic loading rate was doubled compared to P-4, as a result of the shorter *HRT* (10 vs. 20 days). At P-1, the observed *SMY* represented a 76% of the theoretical *SMY* of the influent substrate. Interestingly, despite the shorter *HRT* at P-2, the observed *SMY* was only slightly lower than that at P-1, and represented 72% of the theoretical *SMY*; in fact, the difference was within the SD of the observed *SMY* at P-1 and P-2. This suggests that the substrate utilization efficiency was only slightly affected by shortening the *HRT* from 20 to 15 days when the manure content was 25%. Even more interesting, the difference between observed *SMY* at P-3 and P-4 was not significant ($p > 0.05$), and represented 49% of the theoretical *SMY* of the influent substrate. Likewise, this suggests that substrate stabilization was not affected by decreasing the *HRT* from 15 to 10 days when the manure content was 75%. As expected, the stabilization of VS during the four operating periods of the study followed a similar trend as the observed *SMY*¹, and the most significant difference in the extent of VS stabilization was observed ($p < 0.05$) from P-2

¹The percent of VS stabilization is usually lower than the substrate utilization values (i.e. observed-to-theoretical *SMY*) due to analytical limitations of the VS determination method.

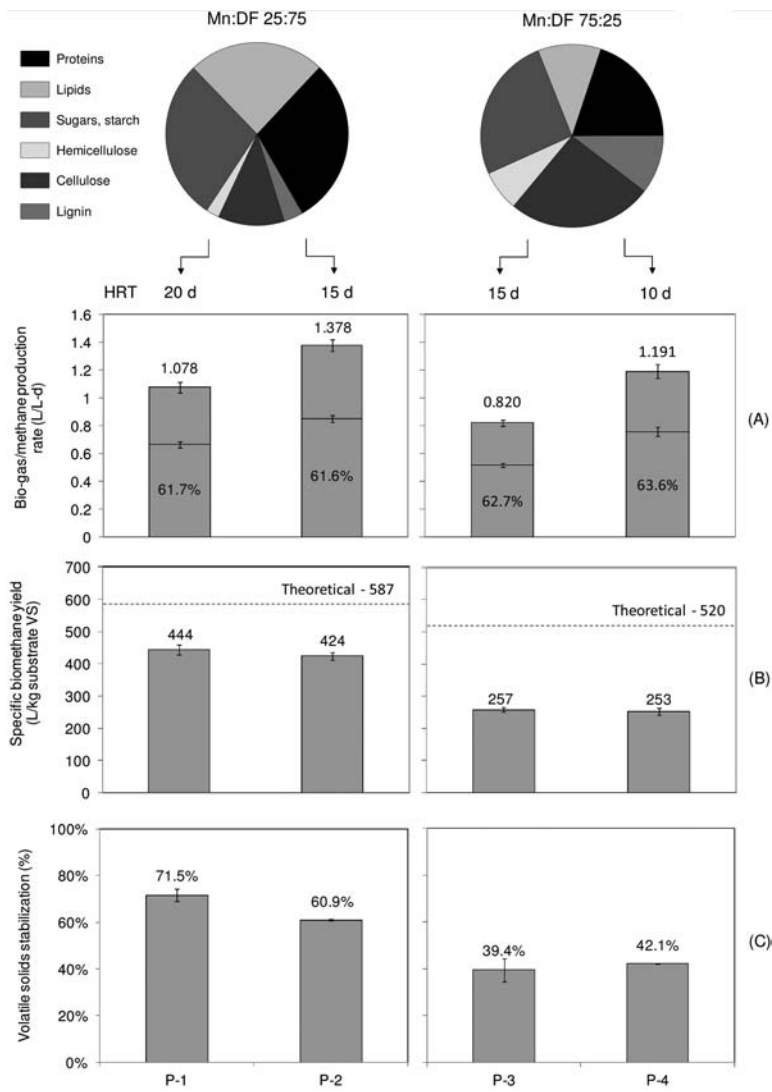


Figure 12.12. (A) Biogas and biomethane production rates (at 0°C and 1 atm), observed specific biomethane yields (at 0°C and 1 atm), and (C) volatile solids stabilization at steady-state conditions during the four periods of the study; percent value in lower bars of (A) indicates the biomethane content in biogas; theoretical SMY in (A) is represented by a segmented line; error bars in (A), (B) and (C) represent the standard deviation of three measurements at steady-state; data from Labatut (2012).

to P-3 (i.e. 60.9% to 39.4%), due to the lower biodegradability of the new influent co-digestion ratio, i.e. Mn:DF 75:25.

12.5 CONCLUSIONS

The physical properties and chemical constituents composing the anaerobic digester's influent will determine the overall biodegradability of the biomass material, and therefore, its extent of stabilization and biomethane production rates.

High-energy, lipid-rich substrates have the potential of producing high biomethane yields per mass loaded to the digester, but their overall biodegradability can be limited by inhibition. Proteins and lignin-free carbohydrates are fairly biodegradable, but have lower energy densities than lipids. However, biodegradability, and thus biomethane yields of protein-rich influents can be limited by potentially inhibitory digestion by-products. Sugar-rich influent streams, such as whey or waste beverages, are easily-biodegradable but usually highly diluted; therefore their biomethane yields are high in terms of their volatile solids portion but low in terms of raw material. More recalcitrant lignocellulosic-materials produce low biomethane yields as a result of their low biodegradability under anaerobic conditions. Their biodegradable fraction and biomethane yields are negatively correlated to their lignin content in a linear model.

In batch co-digestion studies with cow manure and an easily biodegradable multi-component substrate, i.e. dog food, a linear decrease in the biodegradability and specific biomethane yields was observed with an increase in the proportion of lignocellulosic cow manure to dog food. In anaerobic digester studies, influent stabilization and therefore specific biomethane yields were maximized at long *HRT*s and low cow manure-to-dog food ratios. At shorter *HRT*s and higher proportion of cow manure, the stabilization and specific biomethane yields decrease considerably. However, for either co-digestion ratio, biomethane production rates increased at the shorter *HRT*s evaluated.

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CHAPTER 13

Pellet and briquette production

Torbjörn A. Lestander

13.1 INTRODUCTION

Only about 7% of total global energy demands are met by industrial processes for renewable energy conversion. If traditional and small-scale usage of renewables (mostly biomass) is included, this figure rises to about 16% (REN21, 2011). Industrial consumption of bioenergy has increased substantially over the last few decades, and is still increasing. Solid biomass is often densified to produce more uniform and standardized bioenergy commodities such as pellets or briquettes, and a variety of systems for achieving such densification have been developed. The most established of these are pellet presses, briquette presses, cuber presses and screw extruders. In addition, there are some newer systems that are still under development, such as the roller press, the tablet press and agglomerator techniques. This area has been reviewed by Tumuluru *et al.* (2011) and Stelte *et al.* (2012). The most widely used technique at present is pelleting in rotating die presses, see Figure 13.1. The market for pellets is much larger than that for briquettes and a book has recently been published describing their production and use (Obernberger and Thek, 2010).

The densification of biomass into solid biofuels with a relatively uniform shape facilitates its handling, storage, and transport. It also generally improves the flow properties of the solid material, which is important when using it as a feedstock in various energy conversion processes. In addition, better flow properties make it easier to precisely control the quantity of biofuel being fed into a burner or boiler. This is especially true for pellets, which can be transported using pneumatic systems. The availability of densified biofuels with such properties has greatly increased the overall usage of biofuels, and especially wood pellets, in subsidized energy systems. For instance, biofuel pellets now contribute more than 10 TWh of Sweden's annual energy consumption. It has become common for wood pellets to be shipped from North America to Europe; the first such shipment was delivered in 1998.

The worldwide use of renewable energy sources in general is expected to increase in the coming years and biomass is predicted to become one of the world's most rapidly growing sources of energy (EIA, 2011). Around 10 million tonnes of biofuel pellets are sold each year, and this is expected to increase significantly in the near future. Notably, the size of the biofuel market in the 27 member states of the EU alone is expected to increase more than 10-fold by 2020 (Sikkema *et al.*, 2011).

The conventional pelleting process involves the following series of steps: drying, grinding, addition of steam, pelleting, screening, cooling, and storage (possibly with additional screening before shipment to the customer). The process for briquetting is similar. It should be noted that there are a number of variants on this general process. For example, in some cases, whole stems are ground using cutters and disc mills before drying.

13.2 STANDARDIZATION OF SOLID BIOFUELS

The varied raw materials used in bio-pellet production and their diverse properties made it necessary to develop industrial standards to promote the trading of solid biofuels as an international

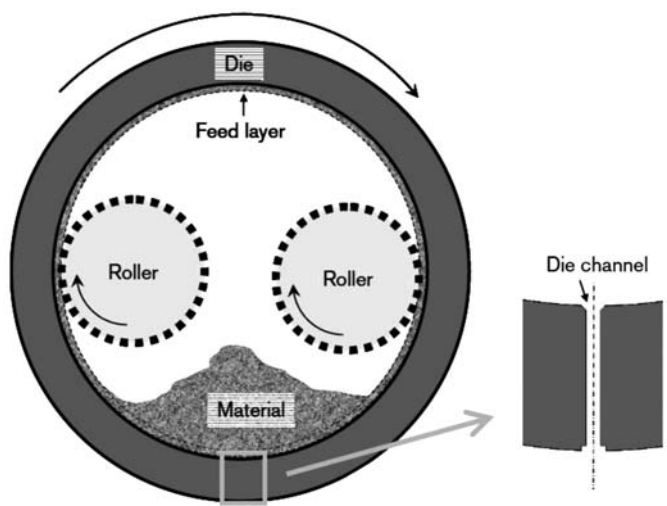


Figure 13.1. Pellet press with rotating die and two free rolling rollers (from Larsson, 2008).

Table 13.1. Specifications of wood pellets (6 or 8 mm in diameter) for non-industrial use. The corresponding European standards are quoted in parentheses.

Property class	Unit	A1	A2	B
<i>D</i> : Diameter, and <i>L</i> : Length (EN 14588:2003)	[mm]	<i>D</i> 06 ± 1.0 3.15 < <i>L</i> < 40 <i>D</i> 08 ± 1.0 3.15 < <i>L</i> < 40	<i>D</i> 06 ± 1.0 3.15 < <i>L</i> < 40 <i>D</i> 08 ± 1.0 3.15 < <i>L</i> < 40	<i>D</i> 06 ± 1.0 3.15 < <i>L</i> < 40 <i>D</i> 08 ± 1.0 3.15 < <i>L</i> < 40
<i>M</i> : Moisture (EN 14774-1 and -2)	[wt%]	<i>M</i> 10 ≤ 10	<i>M</i> 10 ≤ 10	<i>M</i> 10 ≤ 10
<i>A</i> : Ash (EN 14775)	[wt%]	<i>A</i> 0.7 ≤ 0.7	<i>A</i> 1.5 ≤ 1.5	<i>A</i> 3.5 ≤ 3.5
<i>BD</i> : Bulk density (EN 15103)	[kg/m ³]	<i>BD</i> 600 ≥ 600	<i>BD</i> 600 ≥ 600	<i>BD</i> 600 ≥ 600
<i>DU</i> : Mechanical durability (EN 15210-1)	[wt%]	<i>DU</i> 97.5 ≥ 97.5	<i>DU</i> 97.5 ≥ 97.5	<i>DU</i> 96.5 ≥ 96.5
<i>F</i> : Fines (EN 15149-1)	[wt%]	<i>F</i> 1.0 ≤ 1.0	<i>F</i> 1.0 ≤ 1.0	<i>F</i> 1.0 ≤ 1.0
<i>Q</i> : Net calorific value (wet basis) (EN 14918:2005)	[MJ/kg] [kWh/kg]	<i>Q</i> 16.5 > 16.5 <i>Q</i> 4.6 > 4.6	<i>Q</i> 16.5 > 16.5 <i>Q</i> 4.6 > 4.6	<i>Q</i> 16.5 > 16.5 <i>Q</i> 4.6 > 4.6

A1: Stem wood; chemically untreated wood residues
A2: Whole trees without roots; stem wood; logging residues; bark; chemically untreated wood residues
B: Forest plantation and other virgin wood; by-products and residues from wood processing industry; used wood.

commodity. The standards adopted in Europe comprise terminology, classifications, and methods for sampling and testing solid biofuels, and provide definitions of different fuel quality classes as well as specifications for general-purpose solid biofuels. Solid biofuels are classified based on their origin, source (woody or non-woody), the properties of the solid biofuels, their end usage (industrial and non-industrial), and their major traded form (pellets or briquettes). The classification system is hierarchical and includes four subgroups: woody biomass, herbaceous biomass, fruit biomass and biomass blends and mixtures; see EN 14961-1:2010: Solid Biofuels, Part 1 – Fuel specifications and classes – General requirements. Efforts to adapt and combine regional standards into a single global standard are currently underway. For illustrative purposes, the requirements for different classes of pellets are shown in Table 13.1.

13.3 FEEDSTOCK FOR DENSIFICATION

13.3.1 Raw materials

The low bulk density and high moisture content of the raw materials for pellet and briquette production make it difficult and expensive to transport them over long distances. They are therefore generally sourced from areas that are in close geographic proximity to the biofuel production site. All pellet and briquette mills thus operate under unique conditions regarding the short- and long-term supply of raw materials. Moreover, each producer acts independently when sourcing raw materials. As such, there is a wide range of materials that could potentially be of interest for producing refined solid biofuels.

Wood is the most commonly used raw material for producing pellets and briquettes. However, the rapid increase in demand for refined solid biofuels will lead to regional shortages of industrial by-products used in their production such as sawdust and shavings generated during wood processing. As a result, there is great interest in identifying alternative raw materials that can serve as feedstocks for pellet production. This prompted the development of a novel process that uses whole unbarked tree stems with low quality wood (Sundström, 2009), which are a major and underused global wood resource. The use of unbarked trees presents a problem because bark typically has a high ash content, averaging 4.0% by mass for coniferous trees and 5.0% for deciduous species. Conversely, the average ash content for the wood of both tree types is only 0.3% (Oberberger *et al.*, 2006). Furthermore, the highest quality specification defined in the recently adopted European standard (EN 14775) requires that pellets have an ash content of less than 0.7% (based on dry weight). Lestander *et al.* (2012a) have investigated the ash content of the pellets produced from different species and stem diameters when using whole stems as the feedstock. Their results suggest that it may be possible to satisfy this ash criterion by blending stems from different species with different dimensions. In cases where this is impossible, the authors have recommended a partial barking of the stems. Another study by Lestander *et al.* (2012b) conducted at an industrial plant demonstrated that it is possible to produce high quality pellets from fresh whole-stem logs. However, this required careful control over the mixture of tree species in the feedstock material and the moisture content of the material entering the pellet presses. Practical experience indicates that pellets containing large amounts of bark and ash pose problems when burned in typical simple burner cups for household use. As such, when alternative feedstocks are used to produce refined solid biofuels, it is necessary to perform comprehensive testing to identify a suitable market niche for each feedstock blend used.

Agro-based biomass has higher ash content than pure wood and is an important resource in the production of refined solid biofuels. Tao *et al.* (2012) have estimated that by-products such as straw, stalks, bagasse, tops, cobs, husks, pods, shells, bunches and fibers account for about 6,700 million tonnes of residual biomass each year. About 95% of this is residual material from the cultivation of five species: maize, rice, wheat, sugar cane and soybeans. The rest are residuals from the production of groundnuts, palm oil, millet, coconut, coffee, cassava, tobacco, jute and cocoa. Woolf *et al.* (2010) have estimated that the global availability of biomass suitable for energy conversion is about 5100 million tonnes.

The low ash content and high ash melting temperature of pure wood makes it one of the most well suited bio-based materials for heat generation by combustion in simple burner cups and boilers. However, wood is a stiff fibrous material and thus requires relatively large amounts of energy for milling and compression when producing densified solid biofuels. While biomass from herbaceous species is fibrous, its densification seems to require less energy than that of wood overall. On the other hand, it can have a high ash content and the composition of its ash may be such that its melting temperature is low (Vassilev *et al.*, 2010; Boström *et al.*, 2012). Precompaction of herbaceous biomass may facilitate its densification in systems such as pellet presses (Thomas *et al.*, 1997; Larsson *et al.*, 2008).

Overall, the chemical composition of biomass is complex and varied. Consequently, solid biofuels from different feedstocks are suited to different market niches.

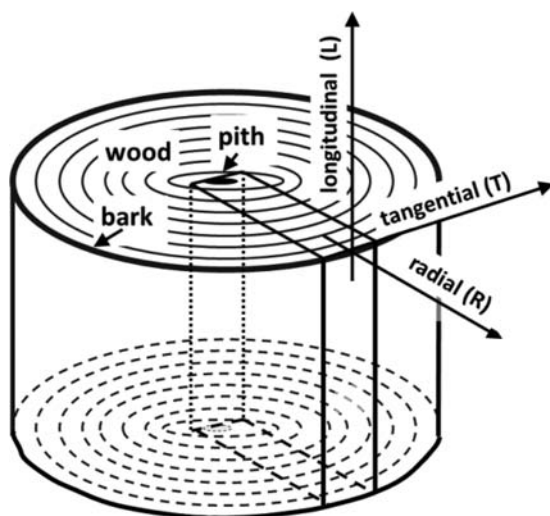


Figure 13.2. The three orthogonal directions used when discussing stem structure.

13.3.2 Biomass has orthotropic mechanical properties

Wood and most other forms of biomass are anisotropic. Most plants also have tissues or structures that have orthotropic mechanical properties. For example, wood has distinct and independent mechanical properties in the longitudinal, radial, and tangential directions (Fig. 13.2), where the longitudinal axis is parallel to that of elongation (along the stem and in the direction of fiber extension) and the radial axis is normal to the growth rings. Nine independent and three dependent constants are needed to describe the elastic behavior of wood: three for the modulus of elasticity, three for the shear modulus, and six for the different Poisson's ratios. Elasticity relates to the ability of the material to recover its initial form after the removal of a load that had induced its deformation. The shear modulus or modulus of rigidity indicates the material's resistance to deflection caused by shear stresses. The Poisson ratio is the proportional deformation along an axis perpendicular to that along which a loading stress is applied. In cases where the loading stress is high, such as during pelletization, biomass particles undergo plastic deformation or failure.

Nielsen *et al.* (2009) studied the influence of wood's orthotropic mechanical properties on the stresses needed to introduce plastic deformation and failure in wood particles during pellet production. They found that the orientation of the fibers in the particles affected their pelletizing properties. Particles (i.e. small flakes that were wide and long but short in height) whose fibers were vertically oriented required less energy to compress and to press through the die channel compared to flake-shaped particles whose fibers were oriented widthwise or lengthwise. The key conclusion drawn from these results was that the method used to produce the particles can affect the densification process.

13.4 PRETREATMENT BEFORE DENSIFICATION

A variety of methods for pretreating disintegrated lignocellulosic materials as a precursor to densification are currently under active investigation, including grinding, pre-heating (e.g. steam addition), steam explosion, ammonia fiber expansion, and torrefaction. Such pretreatments can reduce the energy consumed during the densification process and improve the quality of the final product. However, no matter what pretreatment is used, the material must be dried before it can be densified. In a study of centralized and distributed biomass processing systems, Eranki and Dale (2011) found that distributed processing networks based on the densification of high-yielding

perennial grasses gave higher energy yields and lower greenhouse gas emissions than an alternative centralized system.

13.4.1 Grinding

This approach to pretreatment involves grinding the biomass prior to densification. The preferred particle size and its size distribution depend on the combustion technique to be used. If the pellets are to be used in a facility that burns powders, grinding should result in finer particles, whereas larger particles can be accepted in the solid fuel used in burner cups within the household sector. If the particles are too large, more energy will be required during pressing because the pelletizer will also mill such particles. Grinding increases the specific area of the material; Peleg and Mannheim (1973) have suggested that particle size has a significant effect on binding because powders have a larger surface area and surface energy per unit weight.

Wood pellets are typically produced by hammer milling dried sawdust or shavings. Because these materials consist of relatively small particles to begin with, only a small energy input is required to further disintegrate and grind them. This kind of grinding is more suitable for dry products than for wet ones. Grinding of moist materials can generate blockages in hammer mills (Oberberger and Thek, 2010). A novel process for producing solid biofuels from natural moistened stems has been developed by Skellefteå Kraft AB, Sweden. This process requires disc milling after the chipping of the stems. The process also offers more scope for controlling the size of the particles produced. The number of particles per gram in the resulting pellets is much smaller and fewer fine particles are generated compared to hammer milling of dry materials.

13.4.2 Pre-heating (e.g. steam addition)

Steam is often added just before densification, especially in wood pellet production, to make the wood particles less rigid. The heat from the steam and moisture seems to improve the compression and relaxation of the fibers in the press channels.

13.4.3 Steam explosion

In steam explosion processes, biomass undergoes sudden decompression from high temperatures and high pressures. The wood cell fiber bunches crack up and the lignin is softened. Feeding a pellet press with material directly after this kind of pre-conditioning has shown significant reduction in the amount of energy needed for densification (Oberberger and Thek, 2010). Moreover, the densified product exhibited high mechanical durability and was more resistant to water uptake.

13.4.4 Ammonia fiber expansion

In the ammonia fiber expansion (AFEX) process, biomass is treated with liquid ammonia at moderate temperatures and elevated pressures (Dale *et al.*, 1996). Sendich *et al.* (2008) describe an improved AFEX reactor in which a 1:0.3:0.25 (by mass) mixture of biomass, NH_3 and H_2O is treated for about five minutes at 90°C and 21 atm. After this treatment, the pressure is released. If this occurs rapidly, the fibrous biomass explodes in approximately the same way as happens in the steam explosion process. The evaporated ammonia is recovered and reused and new approaches to ammonia quenching and recovery have been developed. The resulting AFEX-treated biomass is hydrolyzed, reducing the required enzyme loadings when it is used in fermentation systems such as those for producing bioethanol. The AFEX process also alters the properties of the biomass, reducing the amount of energy consumed during its densification and improving its binding properties (Tumuluru *et al.*, 2011).

13.4.5 Drying

Drying of biomass is a necessary step in obtaining a densified product that will be stable during prolonged storage provided that the humidity is relatively low. When densified solid biofuels from natural lignocelluloses are wetted, the particles swell and will fall apart, returning to their original

shape. Furthermore, lignocellulosic biomass is hydrophilic when below its fiber saturation point and will adsorb water vapor from the air if the relative humidity is high enough.

The dryness of the particles to be pelletized is another parameter that has a profound impact on pelletization. It seems that particles of biomass such as wood must retain a few monolayers of water molecules in order to achieve a solid fuel product with the required density and mechanical durability. If the particles' moisture content is too high, they will compress efficiently but also be very elastic. The formation of cylindrical shells has been observed on a few occasions during briquetting when using particles with excessively high moisture content. This may occur because compression of such particles increases the friction between the particles and the wall to the point that it exceeds the particle-to-particle friction. This would cause particles to flow more rapidly in the center of the press channel; the resulting friction would heat the layers closer to the walls.

The water content of raw biomass is often as high as 50–60% (wet basis). Drying is an energy-consuming process (Table 13.2) but can be done at low temperatures. This means that surplus low-temperature (<100°C) and low-value heat can be utilized. There are many industrial facilities that produce surplus heat, such as combined heat and power (CHP) plants that are connected to a district heating system. Such plants are usually designed with top loads to match the demand during cold seasons and can generate surplus heat during warmer months when loads are lower.

Natural drying is the simplest form of drying. For energy grasses such as switch grass (*Panicum virgatum*), reed canary grass (*Phalaris arundinacea* L.) and miscanthus (*Miscanthus giganteus*), this can be achieved by delayed harvesting, i.e. by cropping in early spring rather than autumn (Lewandowski and Heinz, 2003; Adler *et al.*, 2006; Xiong *et al.*, 2009).

Forced drying is necessary in order to reduce the water content of biomass to about 10 wt% (w.b.) during the production of densified fuels. There are many different approaches to such forced drying; the main techniques are listed in Table 13.2.

The most effective system for minimizing the amount of energy consumed during drying would be a series of coupled heat exchangers at progressively lower temperatures, with each one being used for a different drying process.

Wahlund *et al.* (2002) reported a drying process with low energy consumption that used superheated steam generated at a bio-based CHP combined facility. In this facility, biomass is dried in pressurized steam and heat was transferred from the 'dirty' steam to 'clean' steam that was used to generate power. In addition, the heat of condensation of the 'dirty' steam was recycled and reused in the drying process.

13.4.6 Torrefaction

Reviews of biomass torrefaction were recently published by van der Stelt (2011) and Koppejan *et al.* (2012). Torrefaction involves the anaerobic thermal conversion of biomass at temperatures of 200–330°C. During this process, the mass of the treated material decreases by approximately 30% but its energy content decreases by only about 10%. The remaining torrefied product thus has a higher energy value than dry un-treated biomass. This occurs because oxygen is lost from the material more rapidly than carbon due to the rapid decomposition of the reactive hemicellulose fraction. There are several ongoing research programs examining the benefits of using torrefied biomass

Table 13.2. The most used drying techniques in the pellet industry.

Name	Principle	Temperatures	Evaporated water*
Tube bundle dryer	Indirect rotating	80–90°C	1000 kWh/tonne
Belt dryer	Direct moving belt	80–100°C	1200 kWh/tonne
Drum dryer	Indirect or direct rotating drum	300–600°C	1000 kWh/tonne
Superheated steam dryer	Direct pressurized 2–9 bars	115–180°C	750 kWh/tonne

*Values indicate the amount of energy consumed per tonne of evaporated water, as reported by Obernberger and Thek (2010).

in energy conversion systems. However, only a few experiments on densifying torrefied materials have been reported so far. Stelte *et al.* (2011) have shown that using torrefied biomass in place of more conventional material had a negative impact on both the pelletizing process and the properties of the resulting pellet when using a single pellet press. Specifically, the torrefied material generated more friction in the press channel and produced pellets with reduced compressive strength. Analyses of the fracture surfaces of pellets produced from torrefied material indicated that the only bonding within them was due to van der Waals forces and mechanical interlocking of the fibers; there were no signs of cross-linking between polymer strands.

13.5 DENSIFICATION TECHNIQUES

Natural moistened biomass usually has a moisture content of around 50 wt% or more on a wet basis. When dried and densified, the energy density of materials such as wood pellets increases by a factor of 5 or 6. The handling, storage and transport of densified solid biofuels is thus 5 to 6 times more efficient and more economical than is the case for raw biomass (Obernberger and Thek, 2010).

Biomass densification is usually conducted by intermittent compression as the press' rollers force the material from the feed layer into the press channel. The most common technique used in briquetting is based on a piston that presses a certain preset volume of dried biomass into a press channel. Table 13.3 gives an overview of techniques for densification of biomass as reviewed by Tumuluru *et al.* (2011), although it omits some concepts that are currently under development. The most widely used technique involves pelletizing using presses with a rotating ring die and a stationary set of free rolling rollers (usually two; see Fig. 13.1).

Table 13.3. Techniques for densification of biomass into pellets or briquettes.

Densification	Principle	Product		NB
Pellet press	Rotating ring die and stationary set of free rolling rollers	Pellets	Intermittent	Schwanghart (1969), Tumuluru <i>et al.</i> (2011)
Pellet press	Stationary ring die and rotating set of free rolling rollers	Pellets	Intermittent	Tumuluru <i>et al.</i> (2011)
Pellet press	Flat die and rotating set of free rolling rollers	Pellets	Intermittent	Tumuluru <i>et al.</i> (2011)
Briquette press	Hydraulic driven piston	Briquettes	Intermittent	Tumuluru <i>et al.</i> (2011)
Briquette press	Mechanical driven piston; continuously rotating eccentric plunger	Briquettes	Intermittent	Tumuluru <i>et al.</i> (2011)
Cube press	Stationary ring die and one free rolling roller	Cubic formed briquettes called cubs	Intermittent	Tumuluru <i>et al.</i> (2011)
Roller press*	Press nip between two rollers	E.g. almond-shaped briquettes	Continuous	Yehia, 2007 Kaliyan <i>et al.</i> (2009)
Extruder	Screw compaction; single or double screw presses	Various forms of pellets or briquettes	Continuous	Tumuluru <i>et al.</i> (2011)
Tabletizer*	Piston		Intermittent	Tumuluru <i>et al.</i> (2011)
Agglomeration*	Tumbling	Spherical agglomerates	Continuous	Mort 2009 Tumuluru <i>et al.</i> (2011)

*Still in development for biomass.

The free rolling rollers in pellet presses or cube presses are dependent on friction against a compressed and coherent feed layer inside the die ring. If this layer is lost then there will be no production because the rollers do not roll and press additional material on to the feed layer. When this occurs and new material is fed in, the press current will show spikes and brief intermittent production rate spikes. Larsson *et al.* (2012) have studied the stability of this layer and its dependency on temperature. They found that low ring die temperatures yielded more stable feed layers.

13.6 MECHANISMS OF BONDING

The bonding mechanisms of biomass particles with moisture contents suitable for densification under high pressures are complex and not fully understood. The behavior of biomass particles during loading for compaction is much more complex than that of homogeneous powders, and the particles have different deformation characteristics. This is due to the wide range of tissue structures and cell types in plant biomass. Furthermore, the composition of biomass varies in terms of its content of moisture, cellulose, hemicelluloses, lignin, extractives, protein, starch, ash elements, and so on. These also affect the densification process. Overall, much remains to be learned about the compaction behavior of biomass particles, and rheological modeling of the relevant processes is currently at a very early stage.

A common conception (Rumpf, 1962; York and Pilpel, 1973; Sastry and Fuerstenau, 1973; Pietsch 1984, Wood, 1987; Thomas *et al.*, 1997; Briggs *et al.*, 1999; Mani *et al.*, 2002) is that during the early stages of compaction when most of the particles retain their original properties and shapes, the particles are rearranged and become more closely packed. In the second phase (Fig. 13.3), the particles are forced against each other and undergo first elastic and then plastic deformation as the pressure increases. At this stage, particle-to-particle contact increases significantly and van der Waals and electrostatic forces may start to bind particles together. In the final phase, when the volume of the material has decreased significantly, the density of the material is almost equal to the true density of its constituent substances. By the end of the third stage, the deformed and broken particles can no longer change their position. This is due to the decreased number of cavities and increased inter-particle conformity, which reaches approximately 70% according to Tumuluru *et al.* (2011). The fastest reduction in volume occurs as the pressure is increased from atmospheric to 50 MPa, and Stetle *et al.* (2011) have shown that the pellet density increases only slightly as the pressure is raised from 250 to 600 MPa in the final phase of compaction.

Most models for the bonding of particles during densification involve mechanical interlocking, solid bridges and intermolecular force. Mechanical interlocking is partly due to the nesting that

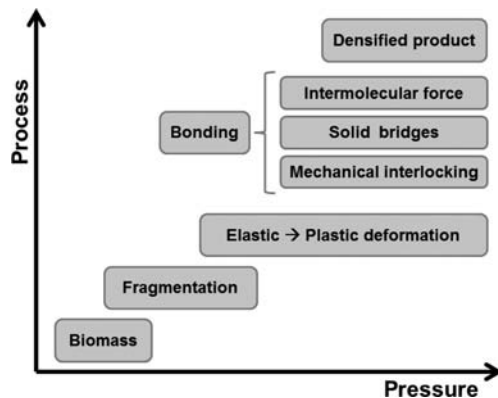


Figure 13.3. Species and processes of importance during the compression of fragmented biomass.

occurs when one or two dimensions of the particles are larger than the third, e.g. needle- or flake-shaped particles. When such particles are compressed, interlocking occurs. Binding is also partly due to solid bridges formed as a result of chemical processes such as the crystallization of dissolved materials, hardening of the binder, hardening of melted substances, etc. “Intermolecular” forces (which may in fact act intramolecularly due to the size of the molecules present in biomass) such as hydrogen bonding are also partly responsible for the binding of compressed particles. For example, hydrogen bonds may form between hydroxyl groups (OH) in adjacent macromolecules as well as between macromolecules and water or between two or more layers of water molecules.

It is well known within the wood pellet industry, and was also shown by Stetle *et al.* (2011), that the greatest pellet stability and integrity are achieved in the moisture content (wet basis) interval of 5% and 15% and that no stable pellets are formed at moisture contents above 20%. A review by Sokhansanj *et al.* (2005) concluded that the optimum moisture content for pelleting fibrous materials is 8–12%. Walker (2006) reported that the presence of water molecule monolayers in wood will yield a minimum moisture content of around 5% (wet basis). To reach the middle of the mentioned interval, i.e. about 10%, multiple layers of water molecules must be formed. (Briquetting can tolerate a relatively high moisture content without sacrificing product quality).

Authors such as Samuelsson *et al.* (2009; 2012) have indicated that there is competition between water molecules and hydrophobic extractives for binding sites in the dried biomass. They also found that the moisture content has significant effects on bulk density and mechanical durability. As such, water molecules play important roles in bonding processes during compaction.

13.7 HEALTH AND SAFETY ASPECTS WHEN HANDLING PELLETS AND BRIQUETTES

The Pellet Handbook by Obernberger and Thek (2010) gives a comprehensive overview of health and safety aspects when handling pellets (and briquettes). Handling and storage of densified biomass can be harmful in many ways, particularly due to its tendency to emit carbon monoxide (CO) and when stored in spaces with poor ventilation. Individuals entering such spaces have suffered lethal accidents, e.g. in the cargo spaces of ships transporting pellets. Svedberg *et al.* (2004, 2008 and 2009) and Arshadi *et al.* (2009) have studied emissions from densified biomass and their health effects. Other hazards that must be considered when transporting, storing, and burning dried solid biofuels include the presence of dust (which can cause explosions), auto-oxidation leading to self-generated fires, and the presence of microbes (e.g. moulds) that can cause diseases.

13.8 CONCLUSION

In conclusion, densification processes such as pelletizing and briquetting are necessary steps in the development of efficient methods for energy conversion. Biomass is a variable and complex material and so its conversion into densified products that satisfy international standards will promote the use of bioenergy as a commodity that can be traded worldwide. Today, almost half of all pellets produced around the world are transported by sea before use. Moreover, refined solid biomass exhibits high flow ability in various handling systems and processes and its energy density is several times higher than untreated raw biomass. Therefore, a future bio-based economy will require the widespread adoption of densified solid biofuels such as pellets and briquettes that can be efficiently handled, stored, and transported.

13.9 QUESTIONS FOR DISCUSSION

- What are the most important factors to control when you briquetize or pelletize?
- What are the most important factors for the economy of these processes?
- How can the economy be improved?
- What type of biomass could be used for pelletization that is not used today normally?

- In what countries is production of pellets and briquettes most important today?
- Where is the highest consumption of pellets and briquettes?
- What is important to get more countries to use this type of products?

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CHAPTER 14

Dynamic modeling and simulation of power plants with biomass as a fuel

Yrjö Majanne

14.1 INTRODUCTION

Biomass refers to any organic materials that are derived from plants or animals. The United Nations Framework Convention on Climate Change (UNFCCC, 2005) has defined biomass as follows:

“A non-fossilized and biodegradable organic material originating from plants, animals and micro-organisms. This shall also include products, by-products, residues and waste from agriculture, forestry and related industries as well as the non-fossilized and biodegradable organic fractions of industrial and municipal wastes”.

14.1.1 Use of biomass as an energy source

Use of biomass as a fuel in electric and thermal power generation has increased remarkably during the last decades (International Energy Agency, 2012). Reasons for this can be found from the issues of climate, energy and labor policies. Mitigation of the climate change has a big role in future energy planning. Emissions of greenhouse gases should be reduced and carbon dioxide neutral biomass-based fuels are an efficient way to retard the increase of CO₂ concentration in the atmosphere.

Biomass combustion covers over 90% of the global contribution to bio energy (van Loo, 2008). The design of a biomass combustion system is mainly determined by the characteristics of the available fuel, local environmental legislation, the costs and performance of the required equipment and the energy and capacity needed (heat, electricity). Effective and environmentally sound use of low-quality fuels with inhomogeneous fuel characteristics such as moisture content, particle size and heating value, requires an expensive fuel-feeding system, advanced combustion technology and a flue gas cleaning system. This is economically possible only in large-scale plants.

Biomass is typically a domestic, local fuel, harvested relatively near the power plant where it is used. That is because of the low energy density of biomasses. Long distance transportation of biomass for energy use is not economically efficient. For this reason, an analysis of available biomass resources is very important in the feasibility study of a biomass-fired power plant investment. Harvesting, transportation and preparation of biomass for energy use requires up to 20 times more employment than e.g. coal and oil (van Loo, 2008). These job positions will be created in the neighborhood of the power plant, and this has a positive impact to the employment situation in the location.

Globally there is a long experience of pulverized coal-fired power plants, but the use and the knowledge of biomass as a power plant fuel is not so well known. However in Finland, for example, biomass has been used already for decades as a fuel in industrial cogeneration power plants in pulp and paper industry and in district heating power plants. Earlier grate combustion technology has been modified to fluidized bed combustion technology mainly during 1980–2000. Nowadays there are tens of biomass-fired fluidized bed boilers, thermal power range from 50 to 600 MW,

operated in industrial and municipal applications producing about 20% of the total electricity and 36% of the total district heat generated in Finland (Finnish Energy Industries, 2012).

14.1.2 Modeling of biomass combustion

The focus of this chapter is on the combustion properties of biomass and how they should be implemented in the dynamic combustion model. General issues of modeling of heat transfer and other phenomena typical for all types of power plants are ignored. They can be found from several sources released in numerous books and articles. The main technology applied in thermal power plants is pulverized coal combustion with wall- or corner-mounted burners. There is a lot of experience and scientific results from this area. Characteristics of biomass combustion differ remarkably from pulverized coal combustion. Properties of biomass result in different types of characteristics of combustion process and technology. One main property of biomass is the variability of properties. Biomass is typically a very inhomogeneous fuel due to its elemental composition, heating value and bulk properties like density, particle size, particle shape, etc. Modern applied technology for biomass combustion in power plant scale is a fluidized bed or a moving grate. Also dimensioning of the furnace and distribution of combustion air differs from coal combustion because of different amounts of flue gases and the dynamics of combustion process. Increased use of biomass as a fuel has been made possible by the research work carried out to define the mechanisms and characteristic properties of biomass combustion. Biomass combustion has been studied thoroughly e.g. in Basu (2006), Galgano *et al.* (2005), Leckner (1999), Raiko *et al.* (2002), Saastamoinen (2004) and Tourunen *et al.* (2004).

The structure of this chapter is as follows: section 14.2 describes the role of simulation in process engineering and requirements set for a good simulation product. Section 14.3 describes properties of biomass as a fuel and section 14.4 introduces the basic principles of grate and fluidized bed combustion. Section 14.5 discusses the modeling principles of biomass combustion and section 14.6 concludes the topic.

14.2 SIMULATION IN POWER PLANT DESIGN AND OPERATION

Simulation is conventionally used for process and automation design and training of operators. Development of computers and software engineering has spread out the application area to real time process control and monitoring, e.g. tracking simulators, predictive simulators for operators decision support system (what-if simulations) and simulators as a part of the optimal process control. Simulation has three significant benefits (Joronen *et al.*, 2007); it enables:

- test runs which cannot be performed with real plant because of economic or safety reasons;
- test runs before the completion of the real physical plant;
- reduction of the work and time needed for commissioning of the plant by enabling the detection and correction of design and configuration errors already during the factory acceptance tests (FAT) before installations and test runs on the site.

Nowadays also a good dynamic performance of the process is required besides steady state properties; emissions and efficiency should be kept inside acceptable limits also during transients and agility is a very valuable property in power generation plants. Increased capacity of non-controllable renewable power generation (wind and solar) has increased the needed capacity and performance of controlled power plants. Thus, process planning based on steady state properties is not enough but also dynamic characteristics of the process should be optimized.

Plant scale dynamic simulations can be used for:

- *Checking the dimensioning of the plant.* Dimensioning of the process equipment is typically based on the required steady state capacity and the experience of the design engineers. How

the requirements of the dynamic performance effect on the dimensioning of the process must be studied with the dynamic simulations.

- *Development and testing of control schemes.* The functionality of the large scale control schemes can be tested only by plant-wide simulations because of the interactions between the sub-processes comprising the total plant.
- *Development of operation strategies.* Dynamic simulation can be used to find cases and to support decision-making where the actions made by the operator are extremely critical for the safety and the economy of the plant.
- *Disturbance and accident considerations.* Simulators can be used to run tests that cannot be carried out with real plant. Simulations can be used to develop systems and policies to improve the recovery from accidents and disturbances.
- *Testing of the automation system.* Factory Acceptance Testing (FAT) by connecting the automation system with the simulator helps to find bugs from the application program before the automation system is installed in the production plant. In addition, controllers can be pretuned and thus the startup time of the new installation can be shortened remarkably.

Simulation is needed also in the design and testing of new process concepts. Simulations give answers to many questions related to the functionality of the proposed concepts. Also developing and testing of new intelligent control methods, e.g. model predictive control (MPC) is carried out with dynamic simulations. In these control methods, dynamic process model is a focal part of the control algorithm and it is a natural part of the commissioning process to use simulation for tuning and testing the application.

14.2.1 Simulation tools

Different types of software tools are applied during the research and development projects to produce information about the properties of the system under development. Balance calculations based on static process models give information about the steady states of the process variables in different operation points. Typical boundary conditions for a power plant process are thermal power of the boiler, temperature of the cooling water and ambient temperature. Balance calculations give answers to questions about how different process configurations and operation points effect on the capacity and the performance of the plant.

Computation fluid dynamics (CFD) tools illustrate how mass and thermal flows behave inside the process as a result of the geometric design of the component. CFD tools help to design the optimal structure e.g. for a power plant boiler to achieve the optimal combustion efficiency and required heat transfer capacity. Boiler manufacturers typically use their own design tools consisting of computation routines for mass and heat transfer and numerous experimental equations to describe the special properties of the process like combustion, heat transfer and emissions.

Information required to build a plant-scale dynamic simulation model is collected from the process configuration, physical dimensions of the process components and pipelines, concept level diagrams of automation application (e.g. PI-diagrams), parameter values and initial values for the process state variables. Thus, the source information is shared partly with the balance calculations and the results of the dimensioning and CFD calculations.

14.2.2 Simulator requirements

The simulation product consists of the computation platform including solvers, model library, etc., and it should have following properties:

- model building should be straightforward and effective;
- effective solvers and model structures resulting in good computation performance;
- robustness of the computation and the model;
- accuracy;
- data protection.

The costs of the simulator consist of the computer equipment, program licenses and working hours needed to build up the simulator. The biggest expenditure is the cost of the required working hours. Thus, the price of the simulator is mostly defined by the effectiveness of the model-building. The price is compared with the benefits when making the decision if the simulation study will be carried out or not. One of the most laborious tasks in model building is the collection of the source information required for the parameterization of the model. Conventionally the simulation project is a separate project from the process design and all the required information for the model building must be collected manually from different sources. This is very time consuming and increases costs. In future this work can be made more fluent by implementing the ISO 15926 standard in all phases of process design. The ISO 15926 is a standard for data integration, sharing, exchange, and hand-over between computer systems. This will lead towards the automatized configuration and parameterization of simulation models.

Robustness of the computation has an important role in the usability of the simulator. Simulation can slow down or stop totally because of numerical problems in the solvers. Computational problems caused for example by an unsuitable numerical integration algorithm, wrong computational parameters (error tolerances, simulation step size, etc.) can lead to numerical instability and excessive noise to the simulation results. Simulation tools may have alternative solvers for different type of problems, for example homogeneous flow model presumes that steam and water are at the same temperature and flow with equal speed. In a multiphase model, different phases are processed separately and water and steam can flow even in opposite directions. The model developer should be accomplished to select the right tools for different problems. In addition, erroneous initial values of the state variables of the model may easily lead to computational problems. Numerical problems may rise also in flow grids, if the single pipe element is defined too small leading to too small pressure difference across the element.

Requirement for model accuracy depends on the purpose and use of the model. In the concept planning phase high accuracy is not required and it cannot even be achieved because there is not enough source information available for parameterizing the model. Individual process components are not defined yet and their exact characteristics are not known. In more detailed analysis, such as checking the dimensioning of the process, high accuracy is required.

A simulation model is an effective way to communicate between project parties. The model helps to point out what kind of results are expected and what the roles and responsibilities of individual parties are. It is clearly beneficial that the model can be used by the whole project team. On the other hand, the model contains detailed knowledge of the developed technology of each supplier, which one would not want to be shown to other parties. Thus, it must be possible to hide this information from the other users without deteriorating the usability of the model.

14.3 BIOMASS AS A FUEL

Biomass combustion involves a number of complex physical and chemical processes. The characteristics of the combustion process depend on the fuel properties and the applied combustion technology. The properties of the fuel influence the combustion process through various fuel characteristics, mainly with respect to fuel moisture, elemental composition, contents of volatiles and char, thermal behavior, density, porosity, particle size and active surface area (van Loo, 2008). Composition and properties of some fuels are compared in Figure 14.1. The increased amount of hydrogen (H) and oxygen (O) in the elemental composition of the fuels increase their reactivity and the increased amount of carbon (C) increases the heat value of the fuel.

Biomass typically contains a high volatile content and low char content compared to coal. This makes biomass a highly reactive fuel. The density of different biomass fuels varies a lot, and a significant difference can be found between hardwoods and softwoods. The porosity of the material influences the reactivity of the fuel by affecting the active reaction surface. Particle size of fuel is an important variable in combustion applications, influencing the steadiness of fuel feeding, dynamics of the combustion process and hydrodynamic behavior of fuel particles in

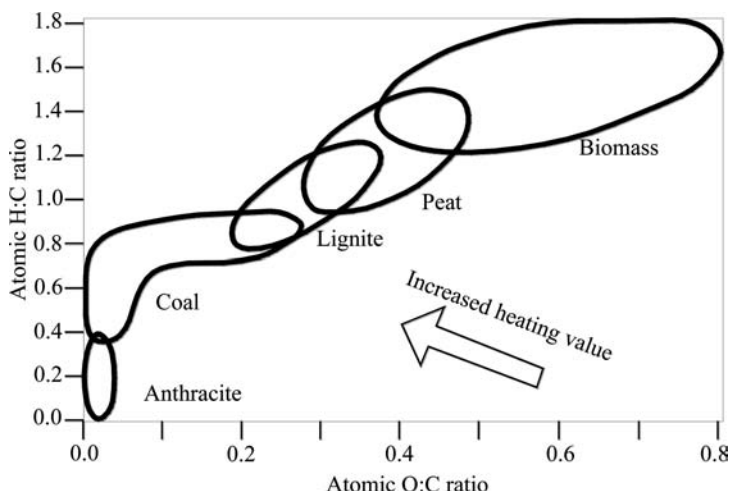


Figure 14.1. Chemical composition of various solid fuels (modified from van Loo, 2008).

the furnace. Smaller fuel particles will need a shorter residence time in the combustion chamber (van Loo, 2008).

Biomass bulk is typically inhomogeneous due to its physical and chemical structures and moisture content. In power plant use, this easily causes instabilities to the fuel feeding process. In fact, one of the biggest problems in biomass-fired power plants is to maintain a smooth and stable fuel power feed into the furnace. The problems are derived from the varying bulk density, lower heating value, and physical structure, like particle shape and size and the amount of splinters.

Also the green parts of biomass, like needles of conifers, cause problems in the use of biomass as a fuel. These green parts have high chlorine contents causing corrosion on hot heat exchanger surfaces. To avoid this problem there exist some additives which should be used together with fuels containing these green parts.

High reactivity and moisture content has an influence on the selected combustion method and the design of the furnace. The chosen combustion method should be able to utilize low heating value fuel and the combustion process should stabilize the disturbances caused by the inhomogeneity of biomass. Fuel feeding points into the furnace and locations of secondary and tertiary air inlets should be designed according to the reactivity of the fuel. High moisture content should be taken into account in the dimensioning of the furnace volume and capacity of flue gas ducts and fans. Combustion methods set limits to the allowed quality variations of fuel. Knowledge about the factors affecting the combustion dynamics is important for designing a well operating combustion control.

14.4 BIOMASS-FIRED POWER PLANTS

A biomass combustion system must be able to burn inhomogeneous low heating value fuels with good efficiency. In a power plant scale, there are two common combustion technologies applied; moving grate furnaces and fluidized bed furnaces. Combustion grates are typically used under 20 MW (thermal) size boilers and in bigger boilers, fluidized bed technology is applied.

14.4.1 Grate combustion

Grate furnaces are appropriate for biomass fuels with high moisture content, varying particle sizes and varying ash content. Mixtures of wood-based fuels, peat and recovered fuels (REF) can be

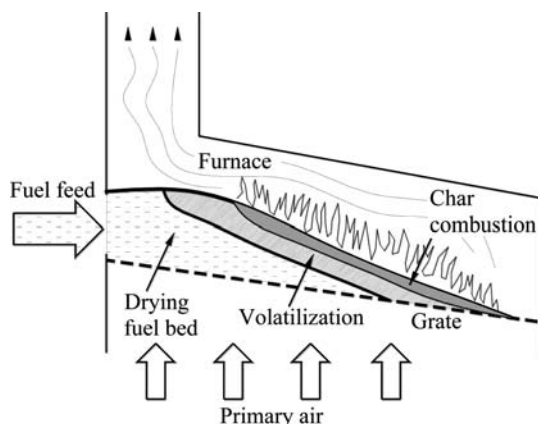


Figure 14.2. Phases of solid fuel combustion on a grate.

utilized. Combustion on grate consists of three phases: drying, volatilization (pyrolyzation) and combustion of the remaining charcoal. The basic structure of the grate combustion is depicted in Figure 14.2. These phases are connected tightly with each other and partly occurring simultaneously in the fuel bed. Preheated primary air passes through the grate and fuel bed, drying the fuel. After the drying, the temperature of the fuel is raised by the furnace heat, and combustible volatile components start to release from the biomass and burn. In the third phase, the remaining charcoal is burned on the grate and the resulting ash is discharged.

A well-designed and well-controlled grate furnace guarantees a homogeneous distribution of the fuel and the bed of embers over the whole grate surface. This is very important in order to guarantee a correct primary air feed over different zones of the grate. Improper air feed may cause slagging, higher fly-ash emissions and increase in the amount of excess air required for a complete combustion, resulting increased flue gas losses (van Loo, 2008). Furthermore, the moving of the fuel bed over the grate has to be as smooth as possible in order to keep the bed of embers stable and to avoid the formation of craters and the elutriation of ash and small unburned fuel particles from the bed to the flue gas flow. The technology needed to achieve these aims includes moving grate structures (reciprocating sloping grate or rotating conical grate), a control system for managing the drying, volatilization and combustion phases by independently controllable primary air flows for different grate sections.

The main problem of the grate combustion control is that the status of the combustion process on the grate cannot be measured directly. Optical pyrometers, cameras with image processing, temperature measurement underneath the grate and pressure difference across the grate and the fuel bed are tested for monitoring the status of the combustion process by detecting the drying, pyrolysis and combustion zones. However, so far any satisfactorily working system has not been developed. With optical sensors, heavy smoke and water vapor in the furnace disturb the measurement process intensely. Temperature measurements of the grate sections suffer from slow dynamics and the interpretation of the information for control purposes is not straightforward. To be able to utilize pressure difference information across the grate and the bed, the grate area should be divided into several individually controllable zones and the air distribution through the grate should be arranged so that the pressure difference across the grate is not too big compared with the pressure difference across the fuel bed. In addition, the interpretation of the pressure difference information is not straightforward for control purposes.

Underfeed rotating grate combustion technology makes use of conical grate sections that rotate in opposite directions. The fuel is fed under the grate to the top of the beehive shaped conical grate by a feed screw. The use of the feeder screw makes it necessary to keep the average particle



Figure 14.3. Underfeed rotating grate. Source: MW Power (2012).

size below 50 mm. The fuel moves smoothly down on the grate with the help of the conical opposite-moving grate sections to the perimeter of the circular grate. The structure of the rotating grate is presented in Figure 14.3. Because of the movement of the conical grate sections, drying and already burning fuels are mixed together helping to burn very wet fuels like bark, saw dust and wood chips with moisture content up to 65% from the wet base. Preheated primary air is fed under the grate through the fuel bed drying the wet fuel and burning the charcoal. The combustible volatilized gases are burned out with secondary air in a separate combustion chamber. Underfeed rotating grate combustion plants are also capable of burning mixtures of solid wood fuels and biological sludge. Dynamic modeling and control of the grate combustion process is described in Kortela and Jämsä-Jounela (2012).

14.4.2 Fluidized bed combustion

Fluidized bed combustion (FBC) systems have been applied considerably in energy production since 1980. Before that, since 1960, the combustion method has been applied to incineration of municipal and industrial wastes. Because of the large heat capacity of the bed material, FBC is suitable for burning wet fuels without any pre-drying. Wet fuel mixes well with hot-bed sand and burning charcoal in the bed, and warms up the fuel to the ignition temperature. Heat capacity stored in the bed also stabilizes the quality variations of the fuel. Regarding technological applications, bubbling fluidized beds (BFB) and circulating fluidized beds (CFB) have to be distinguished. The principle structures of BFB and CFB furnaces are presented in Figure 14.4.

The fluidized bed furnace contains hot, inert granular material, typically silica sand. Primary combustion air, so called fluidizing air, enters the system below the furnace bottom through nozzles and fluidizes the bed so that it becomes a seething mass of particles and air bubbles. Effective heat transfer and mixing provides good conditions for complete combustion with low excess air amount. The combustion temperature has to be kept relatively low in order to prevent sintering of the bed. Typically, the temperature is kept 100°C below the temperature where ash starts to soften. For wood-based fuels bed temperature is typically operated near 900°C. Bed temperature can be controlled by replacing a part of primary air flow with recirculated inert flue gas. Inert flue gas reduces oxygen concentration in the bed and decreases the intensity of combustion and thus the temperature of the bed. In order to maintain the required total air flow into the combustion process, the substituted primary air is added to secondary and tertiary air flows blown into the upper parts of the furnace.

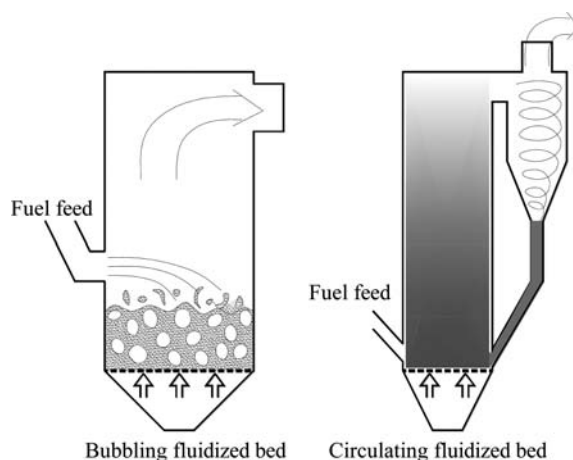


Figure 14.4. Principal structures of bubbling fluidized bed and circulating fluidized combustors.

Due to the good mixing in the bed, FBC plants can deal flexibly with various fuels and fuel mixtures. Due to the variability of both fuel particle size and concentration of impurities contained in the fuel, flexibility is still limited. Therefore, an appropriate fuel handling method for crushing the bigger particles and separation of stones and metals is needed. Another critical issue is related to the use of high alkali biomass like straw and other herbaceous fuels. Due to a low melting temperature, alkali-rich ash may agglomerate, impairing the fluidizing properties of the bed or in the worst case melt down the bed and clog the primary air nozzles.

Low NO_x emissions are characteristic of FBC because of low excess air demand, air staging to primary, secondary and tertiary air flows and relatively low combustion temperature. Because of the small excess air factor, the thermal efficiency of the combustion process is good. It makes the combustion method suitable for large-scale plants. Moreover, the utilization of additives, e.g. limestone for sulfur capture, works well due to the good mixing in the bed. For smaller combustion plants, the investment and operation costs are usually too high in comparison to the grate-fired systems.

14.4.2.1 Bubbling fluidized bed combustion

In bubbling fluidized bed (BFB) furnaces, the fluidized bed remains at the bottom part of the furnace. The primary air is supplied through the nozzles at the bottom of the furnace, and the air flow fluidizes the bed. The bed material is usually silica sand with 1–3 mm diameter size and the fluidization air velocity varies from 0.7–2.0 m/s. Secondary air is fed into the furnace to a so-called splashing region, which is the boundary region just above the bed. For biomass most of the combustion takes place in this region because of the high amount of volatile components released immediately after fuel enters the furnace from the feeding holes above the bed. The rest of the combustion air is fed into the upper parts of the furnace as the tertiary air to burn out the rest of the combustible gases.

BFB furnaces are suitable for burning reactive, low heat value and inhomogeneous fuels with variable particle size. Thus, BFB combustion is very suitable for combustion of biomass and peat. For nonreactive fuels like coal, the problem is that unburned nonreactive fuel may accumulate in the bed causing problems with combustion control. With reactive fuels most of the fuel will volatilize and burn immediately after entering the furnace, and very little will stay in the bed. Accumulation of unburned fuel in the bubbling fluidized bed is problematic also because of an ineffective horizontal mixing in the bed. Occasional fuel rich areas in the bed may cause local

overheating and sintering of the bed. Hydrodynamics and modeling of the bubbling fluidized bed furnaces are described in more details in Galgano (2005) and Oka (2004).

14.4.2.2 Circulating fluidized bed combustion

Compared with BFB furnaces, circulating fluidized bed (CFB) furnaces utilize higher fluidizing air speeds and smaller bed sand particles with 0.2–0.5 mm diameter. Solid bed and fuel particles will be carried by the gas flow to the top of the furnace, where solids are separated from flue gas by a cyclone separator. Solid material is returned back to the bottom of the furnace and hot flue gases flow through convective heat exchange region to the flue gas filters and finally to the stack (see Fig. 14.4). The higher turbulence in the CFB furnace leads to very good heat transfer capacity and very homogeneous temperature distribution in the bed. This is an advantage for stable combustion conditions and the control of air staging.

The disadvantage of a CFB furnace is the higher investment cost compared with the BFB furnace caused by additional components like cyclone separators, return leg and loop seal required for returning the solid material back to the bottom of the furnace. In addition, a more expensive fuel pre-treatment system is needed because of the required smaller fuel particle size. CFB combustion has also a higher dust load in flue gases that should be taken into account when designing the capacity of the electric precipitator. However, a CFB furnace is more flexible with fuel properties; more versatile fuel mixtures and less reactive fuels like coal can be used. Behavior of fluidized bed combustors is described in more detail in, for example, Arena *et al.* (1995) and Oka (2004).

14.5 MODELLING OF BIOMASS COMBUSTION

A combustion process consists of three main phases: warming and drying of fuel, release of volatile components from solid biomass (pyrolyzation) and combustion of remaining charcoal. Whatever the combustion method, these three sub-processes occur and define the progress of the combustion process. In order to be able to model the combustion process the thermodynamic behavior of biomass must be defined during these three phases of combustion.

14.5.1 Thermodynamic properties

Combustion is a thermo-chemical conversion process and the thermodynamic properties of biomass remarkably influence the characteristics of the process. In the beginning some important thermodynamic properties should be described; thermal conductivity, specific heat and heat of formation (Basu, 2010).

14.5.1.1 Thermal conductivity

During all the phases of combustion, biomass particles are subject to heat conduction. Biomass is a highly anisotropic material, which means that the thermal conductivity depends on the direction. Thermal conductivity is better along its fibers than across them. In addition, conductivity depends on the density, moisture, porosity and temperature of biomass. Based on a large number of samples, MacLean has developed the correlation equation to define the dependency of biomass density and moisture to the coefficient of thermal conductivity K_{eff} [W/(K · m)] (Basu, 2010):

$$\begin{aligned} K_{eff} &= \rho(0.2 + 0.004m_d) + 0.0238, \quad \text{for } m_d > 40\% \\ K_{eff} &= \rho(0.2 + 0.0055m_d) + 0.0238, \quad \text{for } m_d < 40\% \end{aligned} \quad (14.1)$$

where:

ρ = density of the of the fuel

m_d = moisture content on a dry basis.

Table 14.1. Formation heat of some compounds (Basu, 2010).

Compound	H ₂ O	CO ₂	CO	CH ₄	O ₂	CaCO ₃	NH ₃
Heat of formation at 25°C [kJ/mol]	−241.5	−393.5	−110.6	−74.8	0	−1211.8	−82.5

14.5.1.2 Specific heat

Specific heat of the material is an indication of the heat capacity. Both moisture and temperature affect the specific heat of biomass. Within a temperature range of 0–106°C, the specific heat of a large number of wood species (dry) can be expressed as:

$$C_{p\theta} = 0.266 + 0.00116\theta \quad (14.2)$$

where temperature θ is in °C. The effect of moisture on specific heat is expressed as:

$$C_p = M_{wet}C_w + (1 - M_{wet})C_{p\theta} \quad (14.3)$$

where M_{wet} is the moisture fraction on wet basis and C_w is the specific heat of water.

14.5.1.3 Heat of formation

Heat of formation (*HF*), also known as enthalpy of formation is the enthalpy change when 1 mole of compound is formed at the standard state (25°C, 101.3 kPa). An endothermic reaction has a positive, and an exothermic reaction a negative, formation enthalpy. Formation enthalpy depends slightly on temperature but in practice in combustion processes this can be neglected. For example, formation enthalpy of CO₂ at 27°C (300 K) is −393.51 kJ/mol and at 927°C (1200 K) it is −395.04 kJ/mol. The formation heat of some typical compounds introduced at the combustion process are listed in Table 14.1.

14.5.1.4 Heat of reaction

The heat of reaction is the amount of heat released or absorbed in a chemical reaction with no change in temperature. In combustion reactions, heat of reaction (*HR*) is called heat of combustion. It can be calculated from the heat of formation (*HF*) as:

$$HR = \Sigma(HF \text{ of all products}) - \Sigma(HF \text{ of all reactants}) \quad (14.4)$$

14.5.1.5 Ignition temperature

Ignition temperature is an important property of the fuel because the combustion reaction can become self-sustaining only above it. According to the Arrhenius law the reaction speed is an exponential function of the temperature. Above a certain point of temperature the rate of heat generation of the combustion process equals or exceeds the rate of heat loss to the environment. This temperature point is called the ignition temperature. The ignition temperature is generally lower for fuels having a high content of volatile compounds. Ignition temperature and the amount of volatile compounds of some fuels are presented in Table 14.2.

14.5.2 Combustion process

After fuel particles have entered the hot furnace, particles start to dry and pyrolyze. After reaching the ignition temperature volatiles and remaining charcoal start to burn. With big fuel particles (diameter > 5 mm) these phases occur simultaneously so that on the surface of the particle, charcoal is already burning while in the inner parts of the particle drying and devolatilization phases are going on. A simplified model of the combustion process is depicted in Figure 14.5.

Table 14.2. Ignition temperature of some common fuels (Basu, 2010).

Fuel	Ignition temperature [°C]	Volatile matter in fuel [dry ash-free%]
Wheat straw	220	72
Poplar wood	235	75
Eucalyptus	285	64
Ethanol	425	—
High-volatile coal	670	34.7
Medium volatile coal	795	20.7
Anthracite	930	7.3

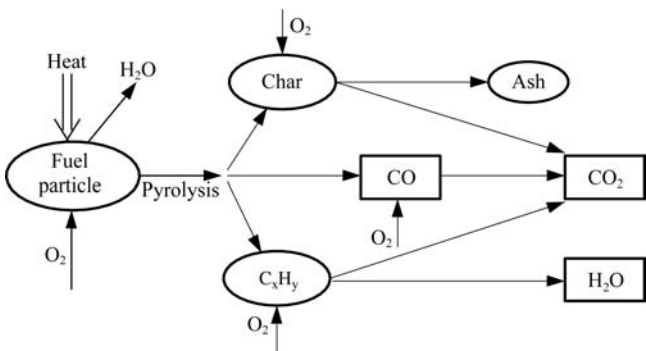


Figure 14.5. Simplified model of combustion.

The combustion process is affected by chemical properties such as reactivity, pyrolyzing temperature, heating value, and structural properties such as particle size, density, porosity, and physical properties such as specific heat and heat conductivity. Progress of the combustion process depends on mass and heat transfer and reaction kinetics. If any of these sub-processes is slower than the others, it will dominate the combustion speed. For big fuel particles, the limiting factor is heat and/or mass transfer.

14.5.2.1 *Drying and ignition*

Drying of fuel starts immediately after the fuel has entered the furnace. The drying speed depends on the applied combustion technology. In grate furnaces drying is slow because the required heat is introduced to the system by primary air supplied below the grate and through the fuel bed and only the a thin surface layer of the fuel bed is exposed to heat radiating and conveying from the furnace. In fluidized bed furnaces, wet fuel particles will be in contact with hot bed sand and the effective heat transfer in the fluidized bed will dry the fuel quickly. In biomass combustion, the proportion of fuel from the total mass of fluidized bed varies from 0.5–5.0% mass percent. Thus, the heat capacity stored in the bed is big enough for drying even very moist fuels. Koistinen *et al.* (1986) have reported that in a 900°C hot bed the drying time for 0.1 mm diameter biomass particles is approximately 0.2 s, for 1 mm particles, approximately 10 s and for 10 mm particles approximately 100 s. Pyrolysis can start just after the drying phase because evaporation of water keeps the particle temperature near 100°C. During the drying phase fuel particles will mix and spread on a wider area in the furnace before ignition. This will smooth and stabilize temperatures in the furnace.

14.5.2.2 Pyrolysis and combustion of volatile components

The pyrolysis process consists of three phases: thermal decomposition (volatilization of solid compounds), transfer of volatile components through the carbon matrix inside the fuel particle and secondary reactions, which can change the composition of the volatile gases.

Heat transfers from the surroundings to the particle and pyrolysis reactions will start after the biomass particle has dried, and its temperature has risen high enough, typically above 200°C. Released volatiles weaken heat transfer from the surroundings to the particle, slowing down the process.

In literature, there can be found reported parameter values for pyrolysis of different types of fuel particles. However, the particle size of biomass fuels is typically so big that besides the reaction kinetics the heat and mass transfer inside the particle should also be taken into account. For this reason, it is more practical to use empiric correlation for dynamic modeling as suggested in Raiko *et al.* (2002). According to this reference, the time constant of pyrolysis reaction t_{vol} can be approximated with the equation:

$$t_{vol} = K_v d_p^n \quad (14.5)$$

where d_p is the diameter of the particle [mm] and K_v and n are parameters. Value of parameter n varies from 1–2 and for millimeter size particles it is 1.5. The value of K_v depends on the temperature and the type of biomass. For milled peat K_v is defined as 1.8 and n is 1.5 (Raiko *et al.*, 2002).

Combustion of volatile components in a hot atmosphere with oxygen is much faster than the pyrolysis process. Typical combustion time for volatile components in a 900°C hot atmosphere is a few milliseconds. In practice, the reaction is not limited by the reaction kinetics but by the availability of oxygen in the combustion zone (Wallen, 2005).

14.5.2.3 Combustion of remaining charcoal

Combustion of charcoal consists of the following steps:

- diffusion of oxygen or other gases from the surrounding atmosphere to the surface of the charcoal particle;
- chemical reaction in the surface of the particle;
- diffusion of reaction products (e.g. CO, CO₂) from the surface of the particle;
- simultaneous homogeneous reaction in the boundary layer.

The combustion speed is typically determined by diffusion of gases to the surface of the charcoal particle or reaction speed with carbon and oxygen or other gases in the surface of the particle. A common interpretation is that surface reactions are dominating for small particles with low combustion temperature, low oxygen concentration of the surrounding atmosphere, and low speed of the surrounding gas. Diffusion mechanisms dominate the combustion speed with big charcoal particles (diameter > 2 mm) if the combustion temperature and the oxygen concentration are high.

Borgman and Ragland (1998) have presented that in the case where diffusion is dominating the combustion speed of charcoal, the combustion time can be expressed as:

$$t_c = \frac{\rho_c d_c^2}{3D_i(\rho_{O_2}(\infty))Sh} \quad (14.6)$$

where ρ_c is the density of charcoal, d_c the diameter of the particle, D_i the molecular diffusion coefficient from oxygen to nitrogen, $\rho_{O_2}(\infty)$ density of oxygen far away from the surface of the charcoal and Sh is the Sherwood number. The correlation equation of the Sherwood number is:

$$Sh = \left[2\varepsilon + 0.69 \left(\frac{Re}{\varepsilon} \right)^{1/2} Sc^{0.33} \right] \quad (14.7)$$

where ε refers to the empty space of the combustion zone (total volume/volume of solids), Re is the Reynolds number and Sc the Schmidt number:

$$Sc = \frac{\mu_g}{\rho_g D_i} \quad (14.8)$$

where μ_g is the dynamic viscosity of gas. The diffusion coefficient can be calculated from the equation:

$$D_i = D_{i_{p_0 T_0}} \left(\frac{T}{T_0} \right)^{1.5} \quad (14.9)$$

where $D_{i_{p_0 T_0}}$ is the diffusion coefficient in the reference state.

Combustion of fine particles is restricted by the reaction kinetics. Combustion time for fine particles t_{cf} can be expressed as (Borgman and Ragland, 1998):

$$t_{cf} = \frac{\rho_f d_f}{1.5 k_c (\rho_{O_2}(\infty))} \quad (14.10)$$

where ρ_f refers the density of fine particle, d_f the diameter of fine particles and k_c is the reaction speed constant. The reaction speed constant is defined by the Arrhenius equation:

$$k_c = A e^{-E/RT} \quad (14.11)$$

where A is the frequency factor and E the activation energy of charcoal combustion, R the universal gas constant and T temperature [K].

Particle size distribution differs in different parts of the furnace. As the combustion process proceeds, bigger fuel particles are fragmenting into smaller ones. Primary fragmentation occurs during the drying and pyrolyzation phase. Bigger fuel particles are fragmented to 2–4 smaller particles due to thermal and mechanical stresses (Scala and Shirone, 2006). The higher the furnace temperature the more probable is the splitting of the particles. After the pyrolyzation, fragile charcoal particles will be fragmented further to smaller particles by mechanical stresses. Fine particles with diameter $< 100 \mu\text{m}$ are produced by collisions of bigger particles (attrition). The speed of production of new fine particles can be expressed by the equation (Basu, 2006):

$$\dot{m}_{att} = K_a \left(u_c - \frac{G}{\rho_{susp}} \right) \frac{m_c}{d_c} \quad (14.12)$$

where $\dot{m}_{att}$ is the attrition speed, K_a is the attrition speed factor, u_c is the speed of charcoal particle, G is the density of solid matter mass flow, ρ_{susp} is the suspension density of fluidized bed, m_c is the mass of big particle charcoal in the furnace and d_c is the average diameter of these charcoal particles.

The combustion model for charcoal consists of dynamic mass balance equations for big and fine charcoal particles and energy balance equations for calculation of heat power released from combustion of both charcoal types. In combustion models, also combustion air supply must be included to model oxygen concentration in different parts of the furnace.

14.6 CONCLUSIONS

Dynamic simulation has an important role in the design of the boiler process itself as well as the control strategy for the boiler. When comparing the biomass fired power plants with coal, gas or oil fired power plants, the biggest difference is in the dynamics of the combustion process and combustion technology. A big challenge in the modeling of biomass fired boilers is to include the varying properties of biomass in the combustion model. This property is needed to estimate how the worst case scenarios in the quality of the biofuel will affect the performance and the controllability of the boiler. Another big challenge is to model the dynamics of the applied

combustion methods. Dynamic behavior of the combustion grate and the fluidized bed is much more difficult to model compared to the operation of oil and gas burners or pulverized coal combustion. Effects of different process variables on the dynamics of the combustion process can only be estimated according to process experiments. Dynamic modeling of biomass combustion processes are too complex for the first principle modeling based on laws of physics and chemistry.

The dynamic model of the power plant boiler consists of the furnace and the combustion models and heat transfer models from the flue gas side to the metal structures of the boiler and onwards to the water-steam cycle of the boiler. The dominating time constants are typically caused by the heat transfer with the massive metal structures of the boiler and by the time required for wet biomass to be dried and ignited. The furnace model consists of mass and energy transfer equations describing the thermal conversion of fuel to heat power in different parts of the furnace. Depending on the applied combustion technology the model should be divided into sub-models describing what kind of activities take place and how much thermal energy is released in different parts of the furnace. A furnace heat transfer model describes how the released thermal energy is transferred to the heat exchangers by different heat transfer mechanisms. In the water-steam side, a thermo-hydraulic solver is used to calculate the transferred heat power from the metal structures of the heat exchangers to the water-steam cycle of the boiler. In the evaporator the solver should be able to handle two phase flows because of the existence of water and steam in the evaporator tubes.

Biomass fired boilers differ from e.g. pulverized coal fired boilers by the combustion properties of the applied fuel. Typical characteristics for biomass are high reactivity, large amount of volatile components, small amount of char, porosity, high moisture content and inhomogeneous bulk properties like particle size and shape. When the heat is released from the fuel by combustion, the heat exchange mechanisms are independent from what kind of fuel the heat is released. Proportional shares of radiative and convective heat exchange depend on the amount of generated flue gas and amount of water vapor in the flue gas, which depend on the used fuel.

This chapter described the special properties of biomass that should be taken into account when modeling the biomass fired power plant. The presented combustion models contain the variables required to model biomass combustion. The models can be parameterized to match the behavior of different types of biomasses. Some of the parameter values can be found from literature and some of them should be determined by process experiments. However, the important issue in modeling and simulation of biomass-fired power plants is the large variability in the characteristics of the fuels applied in real plants. We should keep this in our minds when analyzing the simulation results.

14.7 QUESTIONS FOR DISCUSSIONS

- Discuss what factors you have to consider if you want to get advanced control to operate in a robust way.
- Discuss similarities and differences between controlling BFBs, CFBs, powdered fuel or stokers with respect to control.
- How important is it to have accurate measurements for advanced control?
- How important is it to get good combustion? What effects does poor combustion cause?

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CHAPTER 15

Optimal use of bioenergy by advanced modeling and control

Bernt Lie & Erik Dahlquist

15.1 CURRENT AND FUTURE WORK IN BIOENERGY SYSTEM AUTOMATION

Energy services have a profound effect on productivity, health, education, climate change, food and water security, and communication services¹; lack of access to clean, affordable and reliable energy hinders human, social and economic development and is a major impediment to achieving the United Nations' Millennium Development Goals. Today, 1.4 billion people still do not have access to modern energy, while 3 billion rely on traditional biomass and coal as their main fuel sources. Through resolution 65/158, the United Nations General Assembly has designated the year 2012 as *International Year of Sustainable Energy for All* to encourage increasing sustainable access to energy, energy efficiency, and renewable energy at the local, national, regional and international levels. This initiative will engage governments, the private sector, and civil society partners globally to achieve three major goals by 2030:

- Ensure universal access to modern energy services.
- Reduce global energy intensity by 40%.
- Increase renewable energy use globally to 30%.

In 2009, the European Union adopted the 20-20-20 target², implying 20% cut in energy consumption, 20% cut in emission of greenhouse gases, and 20% increase in renewables share by 2020.

With a growing world population that expects just access to energy for all, it is thus imperative to (i) make use of all realistic energy sources, (ii) distribute sites geographically to increase robustness and security of energy conversion, (iii) make energy available for all through distribution networks, (iv) improve energy efficiency at all levels, and (v) achieving all this in a sustainable way.

Biomass is biological material from living, or recently living organisms. Biomass is thus organic matter derived from plants such as wood from forests, crops, seaweed, material left over from agricultural and forestry processes, human and animal wastes, etc. Biomass has been an important energy source in the past. Although energy is an important factor for improving human conditions, four other factors related to *sustainability* take precedence:

- *Air quality*: humans can only live a few minutes without air/oxygen, and a development that reduces the air quality is not sustainable.
- *Fresh water*: humans can only live a few days without fresh water, and a development that gives insufficient access to fresh drinking water of good quality is not sustainable. Agriculture accounts for about 70% of global freshwater withdrawals from rivers, lakes and aquifers. Growth trends in biomass production will lead to increasing competition and pressures on water resources.³ Still, re-vegetation of deserts and dry land may make better use of the precipitation that actually is there.

¹<http://www.un.org/en/events/sustainableenergyforall/>

²<http://news.bbc.co.uk/2/hi/7765094.stm>

³http://www.unep.org/pdf/water/Water_Bioenergy_FINAL_WEB_VERSION.pdf

- *Food*: humans can only live a few weeks without food, and a development that gives insufficient access to healthy food is not sustainable. Examples of use of crops for biofuel which have led to reduced access to food/increased price for food, or use of agricultural land for biofuel crops at the expense of available land for food, is hardly sustainable when there is a shortage of food/insufficient distribution of food.
- *Slowly changing environment*: Biomass grows by photosynthetic conversion of CO_2 in the atmosphere into carbon; biomass thus constitutes storage of energy from the sun. The growth rate m_{biomass} is essentially proportional to the exposed surface area A of leaves, etc. and the partial pressure p_{CO_2} of CO_2 in the atmosphere, $m_{\text{biomass}} \propto A \times p_{\text{CO}_2}$.⁴ This implies that increased production of biomass for food or energy conversion *either* requires a larger surface area for uptake of CO_2 or a higher partial pressure of CO_2 – but higher partial pressure of CO_2 is undesirable e.g. for climate reasons.⁵ Too extensive harvesting of biomass may lead to soil erosion and the spreading of deserts, etc.

Based on these concerns, it follows that biomass cannot alone solve the need for energy to the world; it is necessary to use biomass in a mix with other energy sources. These other sources may directly convert solar energy to electricity (photovoltaic methods) or heat (e.g. heating water by solar energy), utilize mechanical energy sources created by solar energy (wind, waves, hydropower, etc.), use stored chemical/nuclear energy, use stored heat (geothermal energy, etc.), use stored carbohydrates (fossil fuel), etc. (Michaelides, 2012). Some of these energy sources have a stochastic nature (wind, waves, photovoltaic, etc.) in that the production rate may change swiftly and unpredictably, while others represent stored energy (biomass, hydro power from reservoirs, geothermal energy, nuclear energy, etc.). The energy mix of energy sources with swiftly changing available power and sources representing stored energy, in combination with continuous variation in consumption of power, implies that the efficient management and storage of energy will be more important in the future (Michaelides, 2012).

With the above concerns, and with a growing world population in need of food, it may not be realistic to extensively grow energy plants on land (Michaelides, 2012). However, there is still a considerable unused resource in waste from food production, etc., and with some development and in an energy mix, biomass to some degree may satisfy all of the above-mentioned requirements (i–v). To succeed in converting biomass into useful energy, the following key areas must be dealt with:

- Increasing the efficiency of converting biomass to useful energy through advances in the design of unit processes;
- Developing economically feasible unit processes with low maintenance cost at various scales, from local small-scale systems to industrial large-scale systems;
- Characterizing and preparing feedstock/biomass in a form suitable for storage and distribution;
- Developing automation strategies that enable economically feasible operation with biomass of varying quality, under varying conditions, targeted at the scale of the process and the competence level of the operators, and at low (maintenance) cost.

Thus, specific problems related to biomass can be grouped into three areas: the preparation of suitable biomass feedstock, the design of units for processing the biomass, and the design of systems for operating/automating the production of useful energy from biomass. The more general problems of how to manage an energy mix, how to off-load the use of fossil fuel by capturing and sequestering exhaust gases, and how to distribute the produced energy (gas/chemicals, heat, electricity) are not dealt with here.

In this chapter, the main focus is on problems related to the on-line operation and automation of conversion processes for producing useful energy from biomass. Section 15.2 gives a brief

⁴The proportionality factor depends on the availability of water, nutrients, etc.

⁵Use of fossil fuel introduces carbon into the atmospheric circulation system, and this way increases the partial pressure of CO_2 . But increased growth of biomass *may* shift more of the existing carbon in the circulation system into the atmosphere.

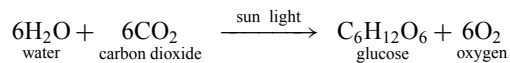
overview of the key processes involved from a control-engineering point of view; in section 15.3 an overview is given of process information in the form of process measurements and process models; in section 15.4 an overview is given of technological challenges concerning operation of the systems; section 15.5 provides a case study on model based diagnostics and control. In section 15.6 the problem of management and integration into product grids are discussed. Some main conclusions are drawn in section 15.7.

15.2 OVERVIEW OF PROCESSES

15.2.1 Biomass

By useful energy, we will mean either energy in the form of heat or fuel, and produced either by thermochemical processes used for biomass with a relatively low content of water, or by biochemical processes used for biomass with a relatively higher content of water. In both cases, it is possible to add units to produce electricity either by using some engine/turbine-generator combination, or directly in a fuel cell.

Biomass can be viewed as stored solar energy, where CO_2 is converted to carbohydrates (e.g. sugars) and stored. In plants some of the biomass is processed further in various ways and may produce waste either from food production or from animals, etc. The two sources of biomass are the purpose-grown energy crops (woody crops and agricultural crops) and waste (wood residues, forestry residues, temperate crop wastes, tropical crop wastes, sewage, municipal solid wastes, and animal wastes/manure):



Biomass can be categorized into wood, grass, fruit, and waste (Kaltschmitt *et al.*, 2009). Plants contain mainly crystalline cellulose (linear polymers of D-glucose, chain length up to 14,000) found in the substance of the framework and the cell walls, hemicellulose (branched polymers of some *hexose*⁶ – glucose, mannose, galactose, but principally *pentose*⁷ – mainly xylose but also arabinose with lower molecular weight than cellulose) has a supporting role in the cell membrane and cements the cell wall, while lignin⁸ (three dimensional network of aromatic polymers with alkylbenzol structure) accompanies the cellulose by cementing and stiffening the plant. Trees typically contain 40–50% cellulose, 18–40% hemicellulose, and 15–30% lignin. Straw and grass typically contain 25–43% cellulose, 14–30% hemicellulose, and 10–20% lignin. The higher level of lignin in trees both makes trees stiffer/harder than grass, and gives trees a higher heating value. In addition, trees contain some fat/lipids (up to ca. 3%) while grass contains protein (nitrogen, up to ca. 13%); biomass also contains a few percent ash (inorganic material). If we consider a mixture of dry agricultural waste, trees, and municipal solid waste, the cellulose fraction ranges from 25–61%, the hemicellulose fraction ranges from 13–40%, and the lignin fraction ranges from 6–30%. A key figure is the pentose fraction, which ranges from 6–28% (Kaltschmitt *et al.*, 2009; Olsson and Hahn-Hägerdal, 1996).

If we break down the biomass into the elements of the dry mass, trees contain 47–50% carbon (C) and grass 43–48% carbon, biomass contains 40–45% oxygen (O) and 5–7% hydrogen (H) – all this is on a mass basis. Furthermore, biomass contains in the order of 1% nitrogen (N), some potassium (K), calcium (Ca), magnesium (Mg), phosphor (P), sulfur (S), and chlorine (Cl), and

⁶Hexose is a monosaccharide with six carbon atoms, having the chemical formula $\text{C}_6\text{H}_{12}\text{O}_6$; a number of different chemical structures exist e.g. D-glucose.

⁷Pentose is a monosaccharide with five carbon atoms, having the chemical formula $\text{C}_5\text{H}_{10}\text{O}_5$; a number of different chemical configurations exist.

⁸From Latin *lignum*, meaning wood.

some traces of heavy metals. The environmental impact of biogas conversion to useful energy is caused by nitrogen, sulfur and chlorine, as well as by trace elements.

Some special types of biomass such as waste from animals (manure) typically have a higher fraction of nitrogen, phosphorous and potassium, e.g. around 5% for each of these components in dry biomass. The remaining dry mass is organic material from dead plants and animals.

In summary, this illustrates that biomass has a considerable variation in quality, and it is imperative to design processes and automation systems that can give efficient operation of converting biomass to useful energy.

15.2.2 Thermochemical processes

The conversion of biomass into useful energy using *thermochemical* techniques can basically be divided into combustion (oxidation) of a fuel, which consists of highly exothermal reactions releasing heat, and a number of (endothermic) processes for refining biomass into more valuable fuel – in principle without using oxygen.

Combustion: *Combustion* takes place in the temperature range of 700–1400°C and is a reaction where the raw material consisting of *gases* such as H₂O (steam), N₂, CO, C_mH_n, H₂, HCN, NH₃, etc. or *solid* carbon C react with oxygen O₂ to produce a flue gas consisting of H₂O (water steam), N₂, CO₂, NO_x, and O₂. Here it has been assumed that carbon in the raw material has been completely oxidized to carbon dioxide CO₂. The released energy (heat) through these reactions of complete conversion to CO₂ is known as the heating value (*HV*) of the raw material; technically one distinguishes between lower heating value (*LHV*; Heizwert) and higher heating value (*HHV*, Brennwert), where the *HHV* > *LHV* and includes released heat from condensing the steam in the flue gas. Assuming dry biomass, the specific heating values can be correlated to the elemental composition of the biomass as e.g. (Kaltschmitt *et al.*, 2009):

$$H_{LHV,d} = 34.8x_C + 93.9x_H + 10.5x_S + 6.3x_N - 10.8x_O \quad [\text{MJ/kg}] \quad (15.1)$$

$$H_{HHV,d} = (1.87x_C^2 - 144x_C - 2802x_H + 63.8x_Cx_H + 129x_N) \times 10^{-3} + 20.147 \quad [\text{MJ/kg}] \quad (15.2)$$

where x_j is the mass fraction of element j in the biomass.

As an example, for corn straw:

$$(x_C, x_H, x_O, x_N, x_S) = (45.7, 5.3, 41.7, 0.65, 0.12) \times 10^{-2}$$

leading to:

$$H_{LHV,d} = 16.43 \text{ MJ/kg} \quad \text{and} \quad H_{HHV,d} = 19.935 \text{ MJ/kg} \quad (15.3)$$

These values calculated from a correlation should be compared to tabulated values for corn straw (Kaltschmitt *et al.*, 2009) being 17.7 MJ/kg and 18.9 MJ/kg, respectively – correlations obviously have a limited accuracy. Typically, the lower heating value of biomass is reported to lie in the interval 16.5–19 MJ/kg, which should be compared to the lower heating value of one liter of mineral oil, being 36 MJ, or ca. 45.0 MJ/kg.

The hot flue gas can be used to heat circulating water (radiation, heat exchangers) in a district heating system, or to produce water steam that heats up the circulating water, or to produce water steam that is subsequently used in a steam engine/turbine to drive a generator that produces electricity. Condensing turbines can achieve an electric efficiency of 25–35%, and are commonly used in electric power plants, while backpressure turbines mainly used in process steam production can achieve efficiency in the range 15–25%; other types may have an efficiency of 10% (Kaltschmitt *et al.*, 2009).

In order to ensure complete oxidation, it is common to add more oxygen than what is stoichiometrically needed. If air is used to supply oxygen, this implies that the flue gas contains

a large fraction of nitrogen and oxygen, and consequently has low fractions of carbon dioxide and other unwanted components (NO_x , sulfur, chlorine, etc.). Using a surplus of air thus makes it more costly to remove these gases, whether for climatic reasons (CO_2 capture) or for reducing the damage to the environment.

Drying: Thermochemical processes work best with dry biomass, and drying at temperatures up to 100–150°C is used to drive out water in order to improve the heating value of the biomass. If the lower heating value of dry biomass is given as $H_{LHV,d}$, the lower heating value $H_{LHV,w}$ of wet biomass can be correlated with the mass fraction $x_w = 0.25$ water as (Kaltschmitt *et al.*, 2009):

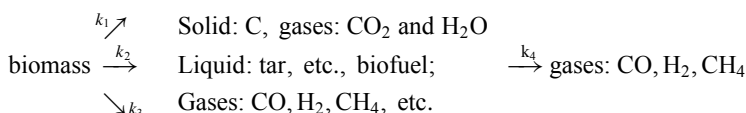
$$H_{LHV,w} = H_{LHV,d}(1 - x_w) - 2.443x_w \quad [\text{MJ/kg}] \quad (15.4)$$

Using the case of corn straw, we see that with a water content of 25%, the lower heating value of wet biomass has been reduced by almost 30%. Drying biomass must strike a balance between sufficient drying and how much energy is put into the drying; the old method of drying biomass in the sun makes good use of solar energy, but may be slow.

Pyrolysis: Pyrolysis⁹ is a thermochemical decomposition of organic material at elevated temperatures *without* the presence of oxygen, leading to irreversible change in both chemical composition and physical phase. The main purpose of pyrolysis is to change the biomass into a fuel that has higher heating value.

Torrefaction (French for *roasting*) of biomass is a mild form of pyrolysis at temperatures in the interval 200–320°C. In torrefaction, intra-molecular drying takes place, and polymers in the lignocellulose start to decompose, thus making the biomass softer and easier to form. Pores start to open up, and trapped traces of gas are released. Torrefaction leads to a dry product with no activity such as rotting, and the decomposition of the lignocellulose makes it easier to produce pellets and briquettes for easy storage and transportation. Torrefaction combined with densification leads to an increase in the lower heating value up to 20–25 MJ/kg.

Pyrolysis at higher temperatures makes the biomass undergo a number of parallel reactions (Kaltschmitt *et al.*, 2009):



At lower temperatures (typically below 400°C), traditional slow pyrolysis reactions with rate k_1 dominate and lead to charcoal, CO_2 and water – the reaction may take up to days. At higher temperatures (400–500°C) reactions with rates k_2 and k_4 dominate and lead to a dark red/brown fluid known as biofuel; biofuel is a mixture of up to 38% water, as well as alcohols, furans, aldehydes, phenol, organic acids, and oligomer carbohydrates and lignin products. The components in the biofuel will react further at rate k_4 and eventually produce a gas mixture containing CO , H_2 and CH_4 . Thus, if biofuel is the desired product, it is important to use a short residence time for the feed: this leads to so-called *fast pyrolysis* (*flash pyrolysis*) where the biomass is heated up rapidly to the reacting temperature (400–500°C) with a residence time in the range of 1s (Wang and Yan, 2008). Finally, at even higher temperatures (up to 600°C), reactions with rate k_3 dominate, leading to a gas mixture containing CO , H_2 and CH_4 .

Gasification: By gasification in the context of biomass is normally meant the reaction of biomass with an oxidizer to produce so-called synthesis gas or *syngas*; syngas is a mixture of carbon monoxide CO and hydrogen H_2 . In practice, gasification takes place under partial oxidation including the use of oxygen as oxidizer; this is however undesired as it increases the less useful CO_2 content of the syngas. Thus, in some sort of ideal gasification, solid carbon (from biomass) reacts with steam where the key reaction is (Figueiredo and Moulijn, 1986):



⁹From Greek *pyr* = “fire” and *lysis* = “separating”.

This reaction leads to other reactions:



Overall, these reactions are endothermic, and it is necessary to heat up the reactor to the operating temperature of ca. 700°C. In the heterogeneous reactions between solid carbon and gas, the reactions will involve diffusion through gas films, adsorption of gas on the solid surface, diffusion through pores in the solid carbon, reaction within the carbon particles, diffusion of products to the surface, transport through the gas film, etc., as well as transport back and forth of heat, and possibly shrinking effects of the particles/build-up of an ash layer (Levenspiel, 1972).

Syngas finds a number of uses. In the simplest case, it can be burnt to yield steam, and thereby heat or electricity using a steam turbine. However, it is more efficient to use syngas as fuel in gas turbines (efficiency 20–45% depending on capacity) or gas motors (30–40%); gas turbines have the advantage of being less sensitive to gas composition. In both cases of gas turbine and gas motor, part of the energy in the high temperature exhaust gas can be recovered e.g. as heated water to yield a total efficiency 80–90% (Kaltschmitt *et al.*, 2009).

The above classifications of combustion, pyrolysis and gasification are not as clear-cut as they appear. We have already seen that biomass contains a large fraction of oxygen, and it is not realistic that true (oxygen-free) pyrolysis takes place: there will be some oxidation due to the oxygen fraction in the biomass. Furthermore, as both pyrolysis and gasification overall are endothermic processes, it is necessary to heat up the reacting medium – this is often done using combustion. If combustion takes place within the reacting medium of gasification, we have *autothermal* gasification. Still, one may try to avoid introducing oxygen into the gasification reaction medium e.g. through heating up some inert mass with high heat capacity (sand, etc.), and then introduce this heat carrier into the gasification reactor leading to *allothermal* gasification. Currently, allothermal gasification is mainly found in laboratory reactors.

To this end, when oxygen enters the reactor, additional combustion reactions take place:



Also, carbon may react with a number of other elements in the biomass, such as nitrogen oxides leading to nitrogen gas N_2 , with sulfur to produce COS, with Fluor to produce CF_4 , etc.

In reality, many practical reactors contain all four stages of drying, pyrolysis, combustion, and gasification. The naming of the reactors is then mainly given by whether the main product is heat, syngas, or charcoal/bio fluid.

15.2.3 Biochemical processes

The other important method for converting biomass into useful energy is *biochemical* conversion, where microorganisms convert biomass typically to ethanol through fermentation, or methane through anaerobic digestion. Biochemical conversion is usually preferred for biomass with high water content. It should be mentioned that microorganism cultures are susceptible to changes over time, e.g. through a change of microorganism type and through mutations.

The first step in biochemical conversion is *glycolysis*, a process where D-glucose (and other types of hexose, $C_6H_{12}O_6$) is broken down into pyruvate (CH_3COCOO^-) in a number of steps taking place in the *cytosol*¹⁰ of the cells of microorganisms, with overall reaction:



where NAD^+ , $NADH$, and ATP are complex molecules important in metabolism. P_i is a phosphorous molecule. Pyruvate is a key component in metabolism, and can be converted biochemically to (i) carbohydrates, (ii) fatty acids, (iii) amino acids, and (iv) ethanol.

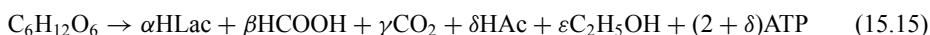
15.2.3.1 Fermentation

Fermentation essentially converts glucose/hexose to ethanol in the *overall* (non-stoichiometric) reaction:



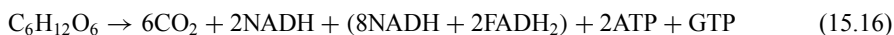
Normally, this conversion takes place in the cells of yeast; yeast works both in an anaerobic state to produce ethanol and in an aerobic state to breed cells/produce heat. Unfortunately, pentose as naturally occurring in biomass ($C_5H_{10}O_5$, aldopentose such as *xylose*; from Greek *xylos* = wood) cannot be converted to ethanol by yeast (Olsson and Hahn-Hägerdal, 1996), and can only be converted very slowly by some bacteria. However, by converting aldopentose to ketopentose (same chemical formulae, e.g. *xylulose*) this enables fermentation to ethanol. Because hemicellulose contains a large fraction of pentose, a key research problem in the economic utilization of biomass lies in effective methods for converting pentose (such as *xylose*) to ethanol (Kuhad *et al.*, 2011).

This overall reaction is composed of the steps leading to glycolysis, as well as parallel steps converting pyruvate to ethanol in anaerobic fermentation and energy/ CO_2 in aerobic fermentation. In *anaerobic* fermentation by bacteria, the glycolysis process will slow down if the cell gets depleted of NAD^+ ; this is solved by Pyruvate being able to react with $NADH$ to recreate NAD^+ : $\text{pyruvate} + NADH \rightarrow \text{HLac} + NAD^+$, where HLac is lactic acid. Other reactions also take place, and the overall reaction starting from *glucose* is:



where HCOOH is formic acid and HAc is acetic acid. If glucose is available at high concentrations, the reaction simplifies to: $C_6H_{12}O_6 \rightarrow \alpha \text{HLac} + 2 \text{ATP}$ (Villadsen, Nielsen & Lidén 2011).

If the microorganism has a functioning *respiration* system, fermentation *via* oxidation can take place. In particular this is valid for yeast, but also for many (but not all!) bacteria. Microorganisms with such a respiration system can switch quickly from anaerobic to aerobic fermentation. The starting point for *aerobic* fermentation is still the decomposition of glucose to pyruvate. However, with oxygen available, NAD^+ can be recreated from oxygen instead of using pyruvate, $NADH + \frac{1}{2}O_2 \rightarrow NAD^+ + \kappa_{NADH} \text{ATP}$, and lactic acid is not produced. The overall reaction from glucose in case of aerobic fermentation is (Villadsen *et al.*, 2011):



Essentially, this means that in aerobic fermentation, glucose is converted to carbon dioxide and breeds the microorganism culture and produces heat.

15.2.3.2 Anaerobic digestion

Anaerobic digestion on the other hand, is often divided into four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The overall reaction can be described as:



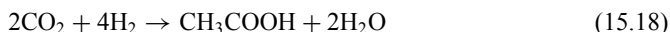
¹⁰The cytosol is the liquid phase of the cytoplasm, the content within the cell membrane but excluding a possible nucleus.

The steps in anaerobic digestion are carried out by anaerobic bacteria, for many of which oxygen is poisonous, and ammonia (NH₃) is an essential nutrient for these bacteria. Phosphorous is also important in the detailed metabolism of each step.

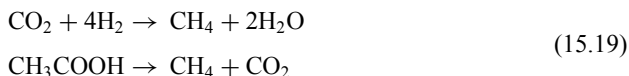
Hydrolysis: Water molecules are in equilibrium $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$, and the hydrogen ion is bacterially used to split polymers into simpler molecules. In hydrolysis of biomass, the result of hydrolysis is that the complex organic molecules are broken down by specialized bacteria into simple sugars (both hexose C₆H₁₂O₆ and pentose C₅H₁₀O₅), amino acids, and fatty acids. *Amino acids* are molecules containing an amine group (with nitrogen), a carboxyl acid group, and a side-chain specific to the particular amino acid. Carboxylic acids have the structure R-COOH, where R is some monovalent functional group. A *fatty acid* is a carboxylic acid with an aliphatic tail.

Acidogenesis: The hydrolyzed compounds are fermented by bacteria into volatile fatty acids¹¹ such as acetic (CH₃COOH), propionic, lactic, and butyric acids, as well as ammonia, neutral compounds (ethanol, methanol), ammonia, hydrogen and carbon dioxide. This step typically produces 20% of the acetic acid that is used for later production of methane, and 4% of the hydrogen used, but these numbers vary with the operating conditions.

Acetogenesis: Various hydrocarbons are converted bacterially to acetic acid, e.g.:



Methanogenesis: Bacterial conversion of various hydrocarbons to methane, e.g.:



15.2.3.3 Biochemical processing

The two main routes for producing refined fuels as discussed above, work well on simple raw materials. However, in particular in the case of biomass from wood or straw, some preprocessing is necessary. A number of possibilities exist:

- Steam explosion: the biomass is heated with steam at 180–200°C and at a pressure of 10–25 bar, whereupon an autohydrolysis of lignocellulose takes place through organic acids released from decomposing hemicellulose. It is possible to mix in liquid sulfuric acid or sulfur dioxide gas into the steam. After some 20 min of treatment, the pressure is suddenly dropped, leading to an explosion of water trapped in the lignocellulose pores, and the resulting physical breakdown of the biomass.
- Acid catalyzed pretreatment: a suspension of lignocellulose with thin sulfuric acid is heated with steam, and then suddenly released.
- Pretreatment by organic solvents such as ethanol, methanol, acetone, etc.

Unfortunately, the use of chemicals in the pretreatment may develop compounds that have an inhibiting effect on the fermentation. In this respect, steam explosion without adding chemicals/sulfur has an advantage. Still, the biomass itself may contain such inhibiting compounds.

The fermentation itself can take place in various types of reactors such as batch or continuous reactors. Because the produced ethanol has an inhibiting effect on the fermentation, the fermentation stops when the ethanol concentration approaches 12% or so. As mentioned, high concentrations of the main substrate (sugars) may also shift the fermentation towards producing lactic acid instead of ethanol. Various minerals/salts are also required for the metabolism to take place. The resulting liquid mixture must then be distilled to separate out the ethanol. Finally, it is necessary to handle the residues such as lignin and (possibly) the xylose part of hemicellulose, etc.

¹¹Volatile fatty acids have smaller molecular weight than general fatty acids, hence they are more volatile.

Anaerobic digestion typically takes place in reactors operating at either ca. 38°C or ca. 57°C, depending on what microorganisms are active, and what is the combined optimal temperature for their operation. The biomass is typically diluted somewhat with water, and it is normally required that there is sufficient nitrogen and phosphorous nutrients in the biomass; the relative amount of these nutrients needs to be at least in a ratio of C:N:P = 100:4:1. This is normally more than fulfilled in the case of animal waste/manure, but not necessarily for other types of biomass. Just like for fermentation, it is possible that some inhibitors are present in the feed; these may have to be removed. Furthermore, the optimal *pH* level may be different for different active microorganisms, and the *pH* level should be monitored and optimized. Ammonia is produced in the digestion, and it is possible that the ammonium level and other concentrations may inhibit the production rates.

15.2.4 Characterization of processes

The preceding sections illustrate that biomass is an important source for producing useful energy in a future energy mix. A number of different technologies and unit processes can be used to produce useful energy from biomass. Biomass is built up of complex compounds, has a relatively large variation in the quality/composition, may hold inhibitory compounds, and require more or less pretreatment before the conversion to useful energy can start. Furthermore, post-treatment is also required to concentrate the product, both in thermochemical processes and in biochemical processes, as well as to handle residuals from the production.

With this process survey, it is possible to give a compact description of problems, possibilities, and methods used to optimize the operation of converting biomass to useful energy.

15.3 PROCESS INFORMATION

15.3.1 Sensors and instrumentation

Sensor and measurement science is essential for getting information about how processes for converting biomass to useful energy operate. A description of how processes operate is often also encoded in mathematical models. The importance of measurements can to some degree be expressed as “without the possibility to compare theory to reality, a mathematical model is only an abstract idea”. However, almost any sensor and measurement technique rely on some mathematical model – a standard mercury thermometer is based on a model for how mercury expands with temperature.

Instead, it is useful to focus on *process information*: we need information about the instantaneous amount and composition of feed, the instantaneous composition of key species (products, inhibitors, etc.) as well as temperature, *pH*, etc. in the pretreatment, reactor, and post treatment steps, we need information about environmental variables that may influence the production, etc. As biomass is a complex mixture, getting information is not an easy task. *Five principles* for collecting measurements are discussed below. Since the different technologies and processes for converting biomass to useful energy are quite different, examples will refer to a reactor for producing biogas through anaerobic digestion.

- (i) Some quantities can be measured with standard sensor technology (Liptak and Venczel, 2003) to yield on-line (continuous or sampled with fixed and short sample time) information. Examples from biogas production are (Kaltschmitt *et al.*, 2009):
 - built-up biogas volume;
 - methane content of produced biogas;
 - carbon dioxide content of produced biogas;
 - hydrogen sulfide content of produced biogas;
 - *pH* level in reactor;
 - temperature in reactor;
 - volumetric feed flow.

Typical for these sensors are that one can buy more or less off-the-shelf sensors that are reasonably well calibrated to physical quantities. Thus, the available electric signals correspond reasonably well to a physical signal such as flow rate, temperature, *pH* level, etc. Furthermore, these are typically single input, single output sensors in the sense that one sensor measures one physical quantity. Although these are more or less off-the-shelf sensors, some of them may require some maintenance and re-calibration, e.g. *pH* level sensors, but also other sensors exposed to a rough environment.

- (ii) Other quantities can only be measured through laboratory analysis. To enable such infrequent measurements to give on-line information, it is necessary to combine the laboratory analysis with a dynamic model using some observer technique (Schuler and Suzhen, 1985). Examples from biogas production are (Kaltschmitt *et al.*, 2009):
 - amount of organic acids;
 - composition of organic acids;
 - content of organic dry substance;
 - content of dry substance.
- (iii) Sometimes, the desired quantity cannot be measured directly. Examples from biogas production are (Kaltschmitt *et al.*, 2009):
 - ammonia content of biogas;
 - acid and base capacity of yeast substrate;
 - content of volatile organic acids and total alkali-carbonate;
 - gas formation test.

In cases where a quantity cannot be measured online, it may be possible to find a correlation between the desired quantity/quantities and other quantities and build a correlation model from the other/indirect measurements and laboratory/temporary measurements of the desired quantities. Three examples, not related to biogas production:

1. By postulating a relationship between pressure measured on-line at 5 different locations in an oil-gas-water separator, $y_{\text{on-line}}$, and measurements of water level, oil level, and oil foam thickness, $y_{\text{off-line}}$, e.g. using a simple, linear model $y_{\text{off-line}} = B y_{\text{on-line}} + e$ where B is a matrix and e is noise, B can be estimated as $\hat{B}$ using on-line measurements of $y_{\text{on-line}}$ and manually recorded values of $y_{\text{off-line}}$. Based on this correlation model, $y_{\text{off-line}}$ can be estimated from on-line measurements as $\hat{y}_{\text{off-line}} = \hat{B} y_{\text{on-line}}$ assuming zero mean noise e . Thus, the desired measurements of water level, oil level and oil foam thickness can be computed from on-line measurements of the 5 pressures and the regression model (Skeie and Lie, 2006). This is an example where several on-line measurements are correlated to several desired measurements.
2. By using clamp-on accelerometers (microphones) in a semi-industrial granulator, it may be possible to correlate the measured acoustic spectrum with e.g. fluidization airflow, reflux of fines to the reactor, granule moisture content, general process states, etc. The acoustic spectrum can be measured by repeatedly measuring, at given time intervals, a continuous but short accelerometer signal sequence, and then compute the Fourier transform, etc. of the signal. Simultaneous controlled measurements of the sought measurements (fluidization airflow, etc.) can then be correlated with the power content of a large number of frequencies in a regression model/calibration procedure (Halstensen *et al.*, 2006).
3. By allowing an image sensor to take repeated snapshots of the flames in a cement kiln, the spectrum of these pictures (2D Fourier transform, etc.) can be correlated with elaborately measured temperatures of the flame. By thus building a regression model/calibrating a model, the spectrum data from the image sensor can later be fed into the regression model to compute the temperature without resorting to the elaborate measurements (Lin and Jørgensen, 2011).

These examples are meant to indicate that only one's fantasy limits which possible types of on-line data can be correlated with the sought information. It is perfectly possible to combine many on-line signals to simultaneously compute several sought quantities. When the on-line signals used as inputs to the correlation model are relatively few (e.g. example (i) above),

a simple principal component regression often suffices. However, when using spectroscopic data as inputs (thus many measured on-line signals), partial least-squared or other regression techniques may give superior correlation models. The examples discussed above are often referred to as *soft sensors*, based on their use of a (calibrated) correlation model to compute the sought signals in software. It should also be noted that in the examples above, it is necessary to calibrate a new model for each process where the model is used, and it may be necessary to re-calibrate the correlation model if the process changes. It would be desirable to find more general correlation models such that a model that has been calibrated for one process could be re-used in another process without re-calibration (Skeie, 2008). This is, however, not trivial.

- (iv) In some cases, process operators are thought to hold useful information about the operation of a plant based on their observation of how the process is running. Often, this may be information that is difficult to quantify precisely in standard sensors. The resulting verbal information from the process operators are sometimes sought to be quantified by combining their information with linguistic/fuzzy logic type models.
- (v) If a dynamic model which describes the physics of the process is available (a *mechanistic model*), then it may be possible to combine any type of previously mentioned measurement or an infrequent laboratory measurement with the dynamic model using a state observer/state estimator to compute physical quantities which cannot be measured in any other way. In order for this to be possible, the mechanistic dynamic model must be *observable* (or at least *detectable*) from the available measurements (Simon 2006).

Typical problems with sensor technology in converting biomass to useful energy is thus to be able to measure the relevant quantities in a complex mixture of compounds, and in harsh environments, and to make the measurements as undemanding as possible regarding maintenance.

A large part of the cost for instrumentation is traditionally related to cabling. Developments in wireless signal transmission may be able to reduce the costs, and may be beneficial in smaller scale systems with little infrastructure for cabling. When connecting sensors to computer systems, it is also important with support for standard protocols such as OPC¹² to minimize the need for special drivers, etc. OPC also makes it possible to access sensor signals over the internet, and provides an infrastructure for storing and reading the data.

15.3.2 Modeling and process description

By mathematical models, we will mean quantitative descriptions of how input signals u are mapped to outputs signals y . Such models can thus be viewed as an encoding of process information, and thus hold process information just as sensor signals/measurements do. Mathematical models are often developed in state space form with additional algebraic equations, e.g. as:

$$\begin{aligned}\frac{dx}{dt} &= f(x, z, u) \\ g(x, z) &= 0 \\ y &= h(x, z)\end{aligned}\tag{15.20}$$

where the state x is interpreted as holding information about the history/current state of the system. Such dynamic models hold information about the inertia of the system, i.e. the resistance towards change. In the modern times of computers, it is common to not compute the value of $y(t)$ at every time instance, but only at discrete time instances t_k . Thus, with computers we only

¹²OPC originally meant OLE for Process Control, but is now based on XML standards and is not considered an abbreviation any more.

compute $y_k \triangleq y(t_k)$, and not $y(t)$ for $t \neq t_k$. Such a discrete time model would be written as:

$$\begin{aligned}x_{k+1} &= F(x_k, z_k, u_k) \\g(x_k, z_k) &= 0 \\y_k &= h(x_k, z_k).\end{aligned}\tag{15.21}$$

15.3.2.1 Mechanistic models

All our information about the world is based on observations, and centuries of science has led to generalizations about how things work. Two key observations are (i) that of causality, i.e. the existence of a time that marches in one direction (the arrow of time), and (ii) the mechanisms that drive the evolution of the world are the same at all times, i.e. physical laws are time invariant. We have already used this information in the model description suggested above: by talking about an input u that causes a response y , we have implicitly assumed causality. And by dropping explicit references to time in our models, we have implicitly assumed time invariant physical mechanisms – if these mechanisms change with time, we would have had to write the models as $dx/dt = f(x, z, u, t)$ or $x_k = F(x_k, z_k, u_k, k)$, etc.

The so-called states in the models above could typically be conserved quantities such as mass, momentum, energy, mass of selected compounds/species, etc. The algebraic equation $g(x, z) = 0$ typically describes phase equilibrium, transport laws, etc. The output equations $y = h(x, z)$ relate the states x and the algebraic variables z to the outputs.

Most systems are more complex than can be captured with the above models, and include a very large number of different compounds/species as well as spatial variation. The above model structures must thus be extended to include partial differential equations (or partial difference models), integral equations (or sum equations), etc. to cover the more general cases.

In summary, the depicted strategy for developing dynamic models based on the accumulated knowledge of mechanisms that drive the evolution of the universe, will lead to what we will call a *mechanistic model*. Sometimes, mechanistic models are denoted white box models, physical models, first principle models, etc. However, mechanistic model is a more generic term, which can also be used in other areas of science such as economics, psychology, etc.

In reality, truly mechanistic models are rarely developed. As an example, many thermodynamic models are based on empirical mathematical mappings, which are basically fitted to experimental data. The same goes for many transport models, reaction kinetic models, etc. Still, in most cases these empirical mathematical mappings have some sort of mechanistic foundation.

Principles for formulating mechanistic models for the process industry are given e.g. in Bird *et al.* (2002), Kondepudi and Prigogine (1998), Taylor and Krishna (1993), Levenspiel (1972), Villadsen *et al.* (2011), Kuuni and Levenspiel (1991), Michelsen and Mollerup (2007) and Ramkrishna (2000). Rawlings and Ekerdt (2002) give a modern, computational approach, while Hangos and Cameron (2001) give some insight into special considerations to be taken for making the models efficient for control computations. However, specialized literature is necessary for developing models for processes for biomass conversion to useful energy.

The above modeling principles will often lead to infinite dimensional/intractable models, and it may be necessary to reduce the dimension/size of the models. In particular, this is true for on-line applications, where it is necessary that the models are at most ordinary differential equations or, in some cases of slow processes, partial differential equations with one spatial variable. A model reduction is often done using model approximation techniques. In model approximation, the solution of $x(t, \xi)$ can be proposed to be written as a finite sum of basis functions, e.g. as:

$$x^*(t, \xi) = \sum_{i=0}^N c_i(t) \varphi_i(\xi, \theta_i) \tag{15.22}$$

where t is time, ξ is some spatial or population variable, and θ_i is some parameter (constant) in the model. Here, $\varphi_i(\xi, \theta_i)$ are known as the basis functions of the approximation;

examples of such basis functions could be polynomials $\varphi_i(\xi, \theta_i) = x^i$, Gaussian functions $\varphi_i(\xi, \theta_i) = \exp(-(\xi - \xi_i)^2 / \sigma_i^2)$ ($\theta_i = (\xi_i, \sigma_i)$), spline functions, *sinc* functions, etc., etc. Functional analysis deals with analyzing the usefulness of various classes of basic functions; good basis functions should lead to $\lim_{N \rightarrow \infty} x^*(t, \xi) \rightarrow x(t, \xi)$, the true solution. Farrell and Polycarpou (2006) show how a large class of modern model classes such as wavelet models, finite element models of various kinds, fuzzy logic models¹³, radial basis neural networks, etc. fit into this model approximation structure.

In the model approximation 15.23 the basis function is chosen by the user, together with θ_i , and we seek to find expressions for $c_i(t)$. The proposed solution structure $x^*(t, \xi)$ is thus fitted to the full mechanistic model e.g. using weighted residual techniques, which essentially implies inserting the proposed infinite sum solution into the model consisting of (partial) differential equations and minimizing a weighted residual in the model. Depending on what type of weights are used, this leads to a collocation solution, Galerkin solution, etc. By truncating the expression of $x^*(t, \xi)$ to a finite number N of basic functions, we thus have a collocation approximation, a Galerkin approximation, etc. The purpose of this approach is thus to reduce the order of the original model, and an ordinary differential model can thus be reduced to a number of algebraic equations, and a partial differential equation can be reduced to a set of ordinary differential equations, etc.

In practice, it is common to allow a number of parameters in mechanistic models to be tunable. Thus, a more realistic model structure is as follows:

$$\begin{aligned} \frac{dx}{dt} &= f(x, z, u; \theta) \\ g(x, z; \theta) &= 0 \\ y &= h(x, z; \theta) \end{aligned} \tag{15.23}$$

where parameters θ are tuned by fitting the model output y to experimental data y^e .

15.3.2.2 Models and model error

In the description so far, there has been a seemingly underlying assumption that it is possible to develop perfect models. Were this true, we would have perfect knowledge of the process behavior as long as we knew the values of all inputs. In practice, a subset u_d of the inputs are given by the system environment – known as *disturbances*, while the rest, u_a are actuator values that we are free to specify. Thus, we could specify desired outputs y_{ref} and compute the necessary inputs u_a to achieve $y = y_{ref}$. In summary: we just need to know u_d , the model, and to specify y_{ref} . Specifically, we do not need to know y .

There are two reasons why this idea will fail:

- We will never have a perfect model description, i.e. the mapping from u to y will at best be known approximately, and
- We will never be able to know all disturbance inputs u_d and the values they have at any time.

This is where the statement that without the possibility to compare theory to reality, a mathematical model is only an abstract idea comes into play. We need to compensate for the lack of model accuracy and the lack of input information by measuring as many disturbance inputs u_d as possible and the necessary outputs y . Then in computing an input u_a which will be used to achieve the desired system response $y \rightarrow y_{ref}$, we need to use these measurements, thus the computed actuator input u_a should at any time use the latest possible knowledge of disturbance inputs u_d and actual outputs y ; we need to make a *feedback* solution where u_a depends on y combined with a *feed forward* solution where u_a simultaneously depends on u_d and y_{ref} .

¹³ Interpreting the membership function as a finite element.

15.3.2.3 Empirical models

The word *empirical* denotes information acquired by means of observation or experimentation. It could be argued that the laws of science developed throughout the centuries are based on observations and experimentation, but it could also be said that these laws have been refined to give a deeper understanding of the mechanisms driving the evolution of the universe. Thus, we will instead use the term *empirical model* to refer to models, which are directly developed from observations and experimentation. Other terms used for empirical models are experimental models, behavioral models, black box models, statistical models, etc.

Empirical models are essentially developed by proposing a model approximation like e.g. below:

$$y_{k+1}^* = \sum_{i=0}^N c_i \varphi_i(y_k, y_{k-1}, \dots, u_k, u_{k-1}, \dots; \theta_i) \quad (15.24)$$

Instead of computing c_i from minimizing some weighted residual, we compute c_i by minimizing a deviation between the model output y_{k+1}^* and experimentally observed output y_{k+1}^e , e.g. by minimizing a least squares measure:

$$V = \sum_{j=1}^{N_e} (y_j^e - y_j^*)^T W_j (y_j^e - y_j^*) \quad (15.25)$$

where W_j is some weighting matrix. Often, we may also add θ_i to the set of tunable parameters in the model, so that we try to compute both c_i and θ_i (Ljung, 1999; Farrell and Polycarpou, 2006).

The main *advantages* of the empirical models compared to mechanistic models are:

- it is not necessary to have a deep knowledge of the physics of the problem;
- in mechanistic model approximations, one may accidentally introduce assumptions that limit how good the model approximation can be – this is to some degree (but not completely) avoided in empirical models;
- it is straightforward to develop software to automate the building of models.

However, empirical models also have a number of *disadvantages* compared to mechanistic models:

- by not utilizing knowledge of the mechanisms of the system, it may be necessary to include a large number of basis functions in the model;
- with a large number of unknown model parameters c_i (and possibly θ_i), this may make it more complicated to compute the unknown parameters, and it poses stricter requirements on the information content of the experiments,
- experiments must be carried out and a new model must be built for every new installation of a process, and even when the same process changes character; it is not possible to re-use models from one installation to the next.

15.3.2.4 Model building and model simulation

Although empirical models are simpler to build, the use of mechanistic models has a number of significant advantages:

- developing a mechanistic model gives a deep understanding of the process, and may also lead to an understanding of how the process can be improved,
- mechanistic models typically have a comparably low number of tunable parameters and a model structure that tries to mimic the mechanism of reality, hence fitting a mechanistic model to experimental data normally requires less of the available experimental data to yield a good model,
- a mechanistic model can to some degree be re-used in new process installations.

These are significant advantages, and to make the model building and reuse of models streamlined, a number of modeling tools exist, e.g. Aspen Plus¹⁴, Aspen HYSYS¹⁵, gPROMS¹⁶, Modelica¹⁷, etc.; specialized simulation tools may exist which are more suitable to studies of biomass conversion. These tools both have support for building models from scratch, for reusing existing models from model libraries, and for carrying out simulation studies. Some of these modeling and simulation tools also have support for model fitting, and even for automating the development of controllers.

In order to fit a mechanistic model to available sensor signals/measurements, extra care must be taken: it is easy to develop a complex mechanistic model where the existing sensors do not hold sufficient information for computing the tunable parameters: the model must be identifiable (Dochain, 2001), or some strategy must be developed for handling parameters that are not identifiable (Brun *et al.*, 2002). It is also advisable to prepare strategies for handling the situation when more measurements become available: in one case of successful use of an on-line mechanistic model, the purchase of new, expensive sensor technology combined with a missing strategy for integrating the new sensor with the model, led to a suboptimal solution.

A number of mechanistic model studies are useful for developing on-line applications for conversion of biomass to useful energy, e.g. for combustion of wood (Branca and Di Blasi, 2003; Porteiro *et al.*, 2006), for drying of biomass (Font *et al.*, 2011; Di Blasi *et al.*, 2003; Peters *et al.*, 2002) for torrefaction (Ratte *et al.*, 2011; Prins *et al.*, 2006; van der Stelt *et al.*, 2011), for pyrolysis of wood (Grønli and Melaaen, 2000; Di Blasi *et al.*, 2001; Galgano and Di Blasi, 2003; Grieco and Baldi, 2011; Di Blasi, 2000; 2002), for gasification of biomass (Lucas, 2005), for fermentation of biomass (Morales-Rodriguez *et al.*, 2011), and for anaerobic digestion of biomass (Haugen *et al.*, 2012).

15.3.3 Monitoring and fault detection

When a process is in operation, it is important to monitor its behavior to make sure that it operates according to specifications. In particular, this is true for processes for converting biomass to useful energy because these are complex processes with complex compounds, with many possibilities for things to go wrong. Fault detection techniques are being developed to detect when a process operates as it should, and when something goes wrong. Such techniques can be based on empirical methods (Monroy Chora, 2012), but can also include mechanistic models to reduce the required amount of data.

In addition to detecting when a fault occurs or when maintenance should be carried out, it is of interest to detect what types of equipment are at fault so that alternative operational strategies can be configured (Kettunen, 2010).

15.4 PROCESS OPERATION

15.4.1 Control and maintenance

Automation of operation is important for the efficient production of products/energy at uniform quality. Here, the main emphasis is not on design of such systems, sequencing of operations, etc., but on on-line operation. The description in previous sections has emphasized the complexity of conversion of biomass to fuel/energy in the sense that the raw material is heterogeneous with a wide variation in content of water, various fractions of polymers, undesired trace elements, inhibitors, etc. With the raw material consisting of hundreds if not thousands of chemical species,

¹⁴www.aspentech.com

¹⁵www.aspentech.com/hysys

¹⁶www.psenterprise.com/gproms

¹⁷<https://modelica.org/>

the chemistry of conversion in itself becomes complex. Possibilities for sensors/measurements are limited, and there is a limited number of actuators.

A key problem is uncertainty in the measurement of feed flow and composition, and even the lack of such information – e.g. in biochemical conversion, summary measurements such as oxygen demand are used. The lack of high quality models such as in electromechanical systems makes it even more difficult to predict the output from the inputs. This implies that feedback control is essential for any realistic operation: feedback control implies using on-line measurements from the output of the system and comparing these to some desired value, to adjust the actuator signals.

It should be noted that feedback control strictly speaking does not need to be automatic; an operator who observes some system state (e.g. color of combustion flame) and by some mental model of the process uses this information to manually adjust the feed flow of air to the system, is in fact operating as a control algorithm in a feedback control loop. However, to make the operation uniform, it is necessary to automate the feedback controller.

The operation can be further improved if information about disturbances such as an approaching rainstorm, observed changes in feed composition, etc. is used actively in a feed forward control structure. Again, feed forward control can also be achieved in manual operation – an operator who observes an approaching rain storm knows that this might cool down a reactor, and thus that it might be beneficial to increase the flow rate of air, is actively performing feed forward control.

Concepts such as open loop control and closed loop control are commonplace. Closed loop control implies using measurements to adjust the actuator signal, and requires feedback control. Strictly speaking, the closing of the loop can be done by an operator carrying out manual feedback control; there is no need for an electric signal closing the loop. Open loop control normally implies using a precomputed input signal or a measured input signal, without using feedback of measured outputs. The concept of open loop control is therefore to some degree a misnomer in that the word *control* is derived from a medieval method of checking accounts by a duplicate register, meaning checking the observed output with the desired output: in open loop control, there is no such on-line checking.

With few measurements and few actuators compared to the complexity of the problem, the *control architecture*¹⁸ of a system is important. The key idea is that for dynamic systems, the available actuators and measurements can *constrain* the achievable performance/efficiency of the system. In many cases, the designer of a control system has some choices e.g. concerning measurements: where in the process should a sensor be placed? With economic constraints – which sensors should be chosen? Choice of measurements may introduce dead-time or inverse response in the system, which may dramatically limit the achievable performance. In the same way, which inputs should be used as actuators, given technological and economic constraints? Actuators may have different ranges of operation, and the key properties of the system may have different sensitivities to different actuators. Furthermore, a property such as inverse response is actually caused by the combination of actuator choice and measurement choice for a specific system.

The control architecture can be studied by using mechanistic models¹⁹ of a system, and it is possible to test different combinations of actuators and sensors through simulation, including the effect of constraints in the inputs, process disturbance and measurement noise. This way, it is possible to find economically optimal combinations of actuators and sensors for good performance of the system (Lie, 1995; Muske, 2002).

The control architecture has some implications for the development of models. For empirical models, this is obvious. However, for the on-line use of models in e.g. state observers and feedback control algorithms, a model should be both observable and controllable. Observability essentially implies that it should be possible to recreate the initial states of a system by combining a sequence

¹⁸As discussed by Graham Goodwin at the Nordic Process Control Workshop in Lund, Sweden, August 2010.

¹⁹Empirical models are less useful for control architecture studies in that a model cannot be built unless real input and output data are available.

of output measurements with the model. Thus, the available measurements determine, together with the model, whether the model is observable. With a fixed set of observations, this in effect limits the usefulness of too complex models. Similarly, the available actuators limit the usefulness of too complex models.

Dynamic models can be used in a variety of ways in controller design. In the simplest case, a simulation model can be used to test out simple control structures such as PI controllers, including a preliminary tuning of the controllers (Haugen, 2010). Effects on the performance of changes in model parameters and input composition can be used to test the robustness of the controller, and possibly change controller parameters to improve the robustness.

The dynamic model can also be used more directly in the controller design, e.g. using a linearized model to develop a robust controller (Skogestad and Postlethwaite, 1996), or directly using the nonlinear model to design a nonlinear controller based upon energy considerations (Dueñas Díez *et al.*, 2008), or in using on-line optimization as in model-based predictive control (Hauge *et al.*, 2005; Maciejowski, 2002).

Processes for converting biomass to useful energy may range in size from local, small-scale systems to regional large-scale systems. The variation in scale has implications on the control design, as large-scale systems will more likely include a higher degree of instrumentation, and be better equipped with sensors and actuators. In addition, large-scale systems will require specialist operators. Small-scale systems will, to some degree, thus require more consideration of the control system design; not only might such systems be equipped with fewer sensors and actuators, but may also lack full shifts of trained operators. This means that it is important to develop control systems, which are simple to use and with a low threshold for understanding the tuning. One possibility is to also use modern technology and allow distant operation through an internet connection, and thus allowing a specialist to tune the control systems from afar.

Some studies on biomass conversion with emphasis on mechanistic models are e.g. within vegetable biomass pyrolysis (Balestrino *et al.*, 2007) and fixed bed gasifier for biomass (Gøbel *et al.*, 2007).

15.4.2 Management and integration into product grids

The main emphasis in the discussion of on-line operation of the conversion of biomass to useful energy has been on the production of heat or enhanced fuels such as biofuel, syngas, ethanol, biogas, etc. A complete range of energy products from biomass conversion to the customer would also include the subsequent conversion to electricity; production of electricity deserves a separate discussion, however. Biofuel will typically be sold through gasoline stations. Heat (including hot water and steam), biogas, and electricity might be used on-site, or be distributed in energy grids such as district heating systems, gas pipes, and electrical grids. In order to facilitate the inclusion of local production of such products, much work needs to be done regarding price policies and technologies. Some work has been done when it comes to local electricity production, e.g. how to integrate micro hydropower plants into the electric grid, how to integrate produced electricity from solar cells into the grid, etc. (Keyhani *et al.*, 2010). More work is needed in this area.

As mentioned in the introduction, various energy sources have a stochastic nature, e.g. wind power, solar power, etc. – the production from these sources can vary rapidly, and cannot be controlled. Other energy sources vary more slowly, but still in an uncontrollable manner, e.g. ocean waves, river flow, etc. Such variation in production is unfortunate for the consumer, who wants reliable access to energy. Other energy sources represent some storage of energy, e.g. stored water in hydropower reservoirs, stored solar energy in biomass, stored heat in district heating pipes, stored electric charge in a network of car batteries, stored geothermal energy, stored nuclear energy, etc. Stored energy may be used to compensate for variations in stochastic energy sources to make the most of the available energy mix. Thus, the management of the energy mix will be important for improving the overall efficiency and availability of energy. Such management must take into account the possibility of using several energy sources/processes and find the best use

by taking into account varying prices and varying consumption (del Mar Pérez-Fortes, 2011). Economic optimization of a mixed portfolio with uncertainty/risk has been used in hydropower production, and may be considered for a general energy mix (Pachamano and Fabozzi, 2010).

One important question is: who should manage the availability of energy? In one case, a utility company offered lower prices to customers if the customer allowed the utility company to cut off electricity in periods of high demand. This might sound like a good deal, but one customer, a hothouse gardener, did not arrange a satisfactory back-up solution, and when the electricity was cut off mid-winter, the annual production of flowers was lost. The advantage of leaving the management to utility companies is that it is challenging for the consumer to manage the energy system. However, the customer has a higher motivation for managing the energy well. To enable customers to manage their own energy consumption well requires the development of inexpensive and user-friendly energy management systems.

15.5 DIAGNOSTICS AND CONTROL USING ON-LINE PHYSICAL SIMULATION MODELS

15.5.1 Introduction

Due to the demanding environmental constraints, efforts have been focused in recent years on improving the efficiency of energy conversion processes. Biomass as a renewable energy source has become a very popular substitute for scarce fossil fuels and contributes to the reduction of greenhouse gases. Biomass is used as fuel in many energy conversion systems; it can be directly fired, co-fired or gasified to produce both heat and electricity. Biomass can as well be converted to be used as a transportation fuel. One of the drawbacks of biomass as a renewable energy source is its heterogenic chemical composition. This characteristic of biomass influences the conversion system efficiency to a great extent.

Dynamic simulation tools are especially useful for fault detection as well as to determine optimal control strategies as described in Venkatasubramanian *et al.* (2003a,b,c). The control requirements for biomass-to-energy processes might become challenging due to the varying composition of the raw material. Dynamic models are useful for fault detection, plant design and operator training; to instruct the plant operators about conventional and emergency procedures, as well as to help them in determining the parameters for optimal plant operation. The combination of physical models with statistical models is an extended approach for decision support (Avelin *et al.*, 2009). The use of dynamic simulation models to determine maintenance operation has earned popularity in recent years as in Ciarapica and Giacchetta (2006).

Energy conversion system models are usually complex models, which require a high structured programming language. Generally, dynamic models are preferred in order to reach a deeper understanding of the process. Many studies have pointed out Modelica as a straightforward object-oriented language developed for modeling of large physical systems (Fritzson, 2007). Dymola is an engineering simulation tool compatible with Modelica language, which provides with the interface to develop the system model. Dymola includes several Modelica libraries for different domains, electrical, hydraulic, thermodynamic, chemical systems, thermo power among others (Otter and Elmquist, 2001). However, this wide range of libraries is not always suitable for the specific application that should be addressed. There are several works where Modelica libraries for power plants (Casella and Leva, 2005) and other energy conversion systems (Salogni and Colonna, 2010) have been developed. In Casella *et al.* (2007), a dynamic model of a biomass-fired-power-plant is presented. In Casella and Colonna (2012), a dynamic model of a gasifier is implemented in Modelica.

In the work performed by Mälardalen University, Modelica component libraries with process components for a biomass fired CFB boiler and an anaerobic digester for biogas production were created. Earlier also a Modelica model for a CFB black liquor gasification process was built. The component models are represented graphically and stored in the designed Modelica libraries.

Once the component models have been defined, the physical connection can be established. The models have been validated towards process data and have been used for fault detection and diagnostics.

The purpose of this work has been to demonstrate the potentials and limitations of the dynamic simulation tools used as well as highlight the possibility of reusing the designed model libraries. The model validation has been made based on process data from full-scale plants.

15.5.2 Approach description

The dynamic simulation approach is presented in Figure 15.1.

The common phenomena for all three proposed energy conversion processes are presented in Figure 15.1. The systematic approach works as following:

- The physical models are implemented in the acausal programming language Modelica.
- Process data from the distributed control system (DCS) is used for validation.
- The proposed simulation tool can be used off-line as well as on-line.
- A comparison between measured values and simulation results for a specific process variable is carried out in order to determine an optimal control strategy or diagnose process upsets.

An on-line application of the proposed dynamic simulation approach has been used in the simulation of a CFB boiler. Here the connection between the DCS and the simulation model is established with Simulink, allowing better control of the signal processing between simulation and the process database. On the other hand, the anaerobic digester model has been running off-line. The input signal into the digester block is generated using the Modelica standard library block “TimeTable” which receives a table of time and values and generates them into an output signal (can be discontinuous if the same time is given two values).

15.5.3 Boiler

The CFB boiler model includes the combustion section as well as water/steam and exhaust gas train. The model is validated towards real plant data and is capable of successfully predicting operation performance. An exhaustive description of this model can be found in Sandberg

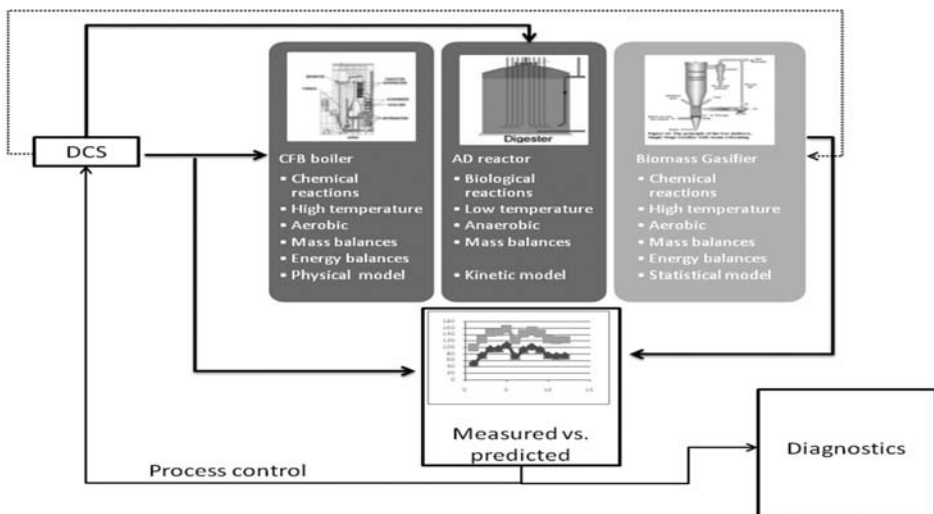


Figure 15.1. Dynamic simulation approach.

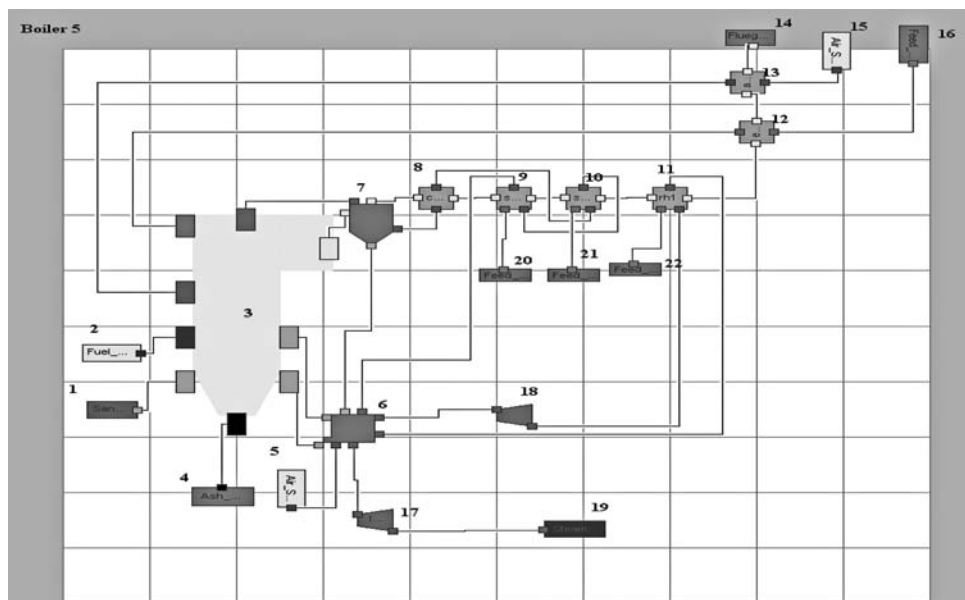


Figure 15.2. View of the CFB boiler in Dymola. Showing boiler 5 at Mälarenergi CHP plant.

et al. (2011). During 2010 and 2011, the model was used on-line at Mälarenergi AB (local power and heat generation plant in Västerås, Sweden) for diagnostic purposes. The components of the Modelica/Dymola model can be seen in Figure 15.2. The components are as follows: 1. Air flow to boiler, 2. Fuel flow and composition, 3. Boiler/reactor, 4. Ash flow, 5. Air flow to Intrex, 6. Intrex–fluid bed where solids come down from cyclone and is heat exchanged towards steam, 7. Cyclone separator where larger particles are separated but also gas cooled, 8. The heat exchanger in the walls of the cyclone where gas is cooled towards steam, 9–11. Steam heating, gas cooling, 12. Economizers where feed water is heated and evaporated, 13. Air pre-heating, 14. Exhaust gas flow and composition, 15. Air flow to pre-heater, 16. Feed water flow, 17–18. Steam flow and temperature/pressure to turbine, 19. Electric power produced, 20–22. Feed water injection to heat exchangers. There are three mass inventories in the model: (i) gas in the boiler including the bed material, fuel etc.; (ii) bed material and gas in the so called Intrex, a bubbling bed below the cyclones where separated sand is fluidized and cooled in two super heaters before the sand is re-entering the CFB boiler; (iii) the steam system with water and steam.

Biofuel, air, sand and material from the Intrex are fed to the boiler, while ash and flue gas including sand and dust is leaving the bed. In addition, heat is transferred to the steam system in the boiler, in the separators (cyclones), in the Intrex and in a series of heat exchangers in the exhaust gas train. Temperature, gas composition and flow rates are measured all the way through the boiler and exhaust gas train and in the steam system. These measurements are then compared to the values predicted from the simulation using the same input data. This includes fuel flow, fuel composition, air flow and feed water flow to the steam dome. Unfortunately, the fuel composition cannot be measured; if moisture content varies, the impact will be significant.

The equations used are primarily stoichiometric calculations of how the biomass is converted through combustion, giving adiabatic temperature and cooling through heat transfer and through transport of material from the boiler combustion zone. The mass in the bed inventory by time is given from:

$$\frac{\partial m_{\text{inventory}}}{\partial t} = \sum m_{i,\text{in}} - \sum m_{i,\text{out}} \quad (15.26)$$

where $m_{i,in}$, is the mass input flow of each single component of the composition vector $i = (C, H, O, N, CO_2, H_2O, NO_2, \text{ash})$ and $m_{i,out}$ is the corresponding output flow. The change in concentration of each component is given by c_i in the bed inventory:

$$\frac{\partial c_i}{\partial t} = \frac{\sum (c_i \cdot m_j)_{in} - \sum (c_i \cdot m_k)_{out}}{m_{inv}} \quad (15.27)$$

where j are all incoming flows and k all outgoing flows of the inventories. Except the bed inventory, we also have one inventory for the Intrex and one for the steam system. The steam system has only water and steam components, while the Intrex has the same components as the bed. The temperature $T_{inventory}$ in the inventory is calculated from the energy balance:

$$\frac{\partial T_{inventory}}{\partial t} = \frac{\sum T_j \cdot cp_i \cdot c_i \cdot m_{j,in} - \sum T_j \cdot k \cdot cp_i \cdot c_i \cdot m_{k,out} + \Delta H - U \cdot A \cdot (T_{inventory} - T_{outside}))}{m_{inventory} \cdot \left(\sum c_i \cdot cp_i \right)} \quad (15.28)$$

where ΔH (enthalpy) is the energy released during combustion and U is the overall heat transfer coefficient, A is the heat exchanger area and $T_{outside}$ the temperature at the other side of the heat exchanger surface (steam temperature vs. exhaust gas temperature). cp_i is the heat capacity for each component i .

The correlations describing the change in each single component are also included in the model. Carbon, C, in the biomass is combusted to CO_2 , and the hydrogen is forming H_2O . Oxygen, O, in the fuel is used for the combustion aside of the oxygen in the air. N, in the fuel is assumed oxidized to NO_2 partly, as a function of oxygen surplus and temperature. Separation of sand is performed in cyclones and cooling in heat exchangers with gas to gas, gas to steam or gas to water transfer. We have not included inventories in the heat exchangers as the residence time is very short.

15.5.4 Other energy conversion processes

The anaerobic digester model describes the process using kinetic equations and mass balances. The main block in the model is the digester block consisting of 22 equations. The model assumes the hydrolysis as the limiting rate or limiting step of the process and describes the hydrolysis using first-order kinetics. The model is validated against process data from a full-scale biogas plant, Vaxkraft in Vasteras, which uses organic municipal solid waste, grease trap sludge and silage as substrate.

For high temperature gasification, we have similar reactions to the anaerobic digester, but a process configuration being very similar to the boiler application.

The energy and material balances are principally modeled in the same way for the anaerobic digestion and the boiler. In the boiler model, the combustion is handled by the conversion of C and H into CO_2 and H_2O while we have a more complex situation for the anaerobic digestion. Still, the final products are mainly CO_2 , H_2O and CH_4 from the anaerobic digestion.

This can be modeled as an extension of equation (15.28):

$$\frac{\partial c_i}{\partial t} = \frac{(\sum (c_i \cdot m_j)_{in} - k \cdot [c_i]^a) - \sum (c_i \cdot m_k)_{out}}{m_{inv}} \quad (15.29)$$

where k is a reaction constant and a is an exponent giving the non-linearity of the conversion. For components being removed c_i is decreasing while for those being created it is increasing. This is for a certain volume element that can be the complete reactor or a smaller part of it.

Table 15.1. Comparison between simulated and measured data. Measured data at two different times and in parenthesis the simulation results.

$T_{s,bSh1}$	$T_{s,aSh1}$	$T_{s,aSh2}$	T_{b1}
376	473	489	842
389	475	498	869
(413)	(469)	(488)	(879)

Table 15.2. Measured process data (DCS) compared to predictions made with the simulation data.

Variables	DCS	Prediction	Error%
<i>Part load (July 5, 2011) at 6.2 kg/s fuel, 30.1 kg/s air flow and 24 kg/s feed water flow</i>			
Steam temperature after HPSH2 [°C]	434	439	1.0
Flue gas temperature after cyclone [°C]	550	566	2.9
Flue gas temperature before cyclone [°C]	551	576	4.6
Steam temperature after cyclone [°C]	366	353	−3.6
<i>Full load (September 2011) 16.5 kg/s fuel, 79.8 kg/s air, 48.8 kg/s feed water</i>			
Steam temperature after High Pressure Super Heater 2 [°C]	494	488	−1.2
Bed temperature [°C]	833	879	5.2
Flue gas temperature before cyclone [°C]	758	757	0
Steam temperature after cyclone [°C]	385	379	−1.5

15.5.5 *Model validation and results*

The boiler simulation model was verified towards process data. In Table 15.1 we can see one set of data.

The steam temperature before the superheater 1 ($T_{s,bSh1}$) is slightly higher in the simulation compared to what is measured, while the temperature after superheater 1 ($T_{s,aSh1}$) is similar, as well as after superheater 2 ($T_{s,aSh2}$). The bed temperature (T_{b1}) is measured in eight positions, varying between 804°C and 869°C. The simulation temperature is 879°C, which is satisfactory, considering the variability of the bed temperature. This temperature variation can be addressed to combustion of particles in the separator, which is not assumed in the simulation model. The fuel moisture content can as well be addressed as a reason for the bed temperature variation. However, in this case the bed temperature would be slightly lower.

In Table 15.2, a comparison between measured and predicted data from the simulation for full load and partial load is presented.

As can be seen the absolute error varies between 0 and 5%. If the purpose of the simulation model would be to have an as accurate model as possible, this might be problematic, but in this case we want to compare the model prediction with measured data many times in a time series to determine the trend. Similar verifications have been performed for the anaerobic digester and a pilot black liquor gasification process. In Derbal *et al.* (2009), Donoso-Bravo *et al.* (2011) and Lübken *et al.* (2007) other anaerobic digestion models are described including verification of the models.

In Figure 15.3, the improvements in the biogas production from first quarter 2006 to last quarter 2010 are depicted. This was the result of several different actions including modeling of the process to get a better understanding of how to control the process in a better way.

15.5.6 *Discussion*

On many occasions, energy conversion processes are based on the same physical laws and can be therefore modeled in similar ways. The construction of a Modelica energy conversion library,

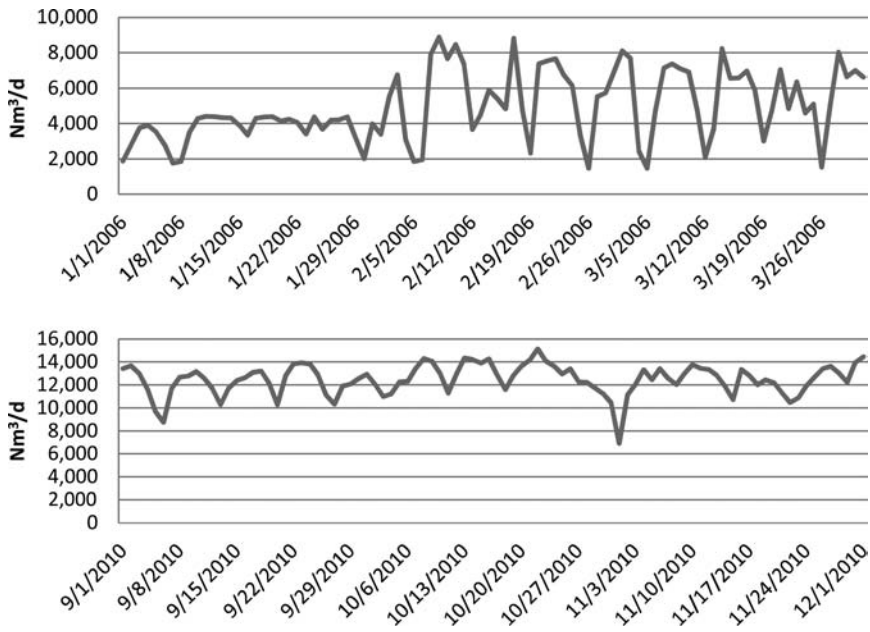


Figure 15.3. Biogas production 2006 compared to 2010.

allows reuse of the designed classes. This means that with not so much effort new energy conversion processes can be modeled. Figure 15.1 shows the similarities and differences between three energy conversion processes that can be considered as completely different processes but with many synergies with respect to modeling.

A dynamic simulation approach has been proposed. This approach has been used for the simulation of energy conversion processes for diagnostics and process control. The use of the advanced object-oriented language Modelica has considerably reduced the modeling efforts thanks to the reusability of the system components and interchange ability between processes. The main feature of the proposed modeling and simulation approach is that the chemical composition of the fuel and other sub-products can be followed through the whole process. As previously stated, the heterogeneity of the incoming raw material is the cause of a multitude of process upsets, making the proposed approach interesting.

The comparison of the simulation results with the real process results allows determining process upsets. The physical models can be combined with other types of models like here Bayesian nets or Multivariate models to obtain a decision support and prediction tools as in Widarsson and Dotzauer (2008).

15.6 CONCLUSIONS AND QUESTIONS FOR DISCUSSION

To achieve the important and fair goals of United Nations and governments regarding availability of sufficient energy for everyone, all energy sources may be considered for use in an energy mix. This energy mix must be managed in such a way as to handle varying consumption and varying energy production in the best possible way. In addition to producing energy, it is also important to distribute the energy to the users.

Converting biomass to useful energy is important, both because it is a renewable energy source and because is available almost everywhere. This distributed conversion of energy both helps to

make energy available locally, and it reduces the vulnerability of few and centrally located energy sources.

Biomass consists of a large number of complex compounds, with a relatively large variation in its composition. During conversion, complex and only partially known reactions take place. Feedback control is thus a key technology to enable efficient energy conversion; feedback necessitates the availability of on-line process information in the form of measurements. However, to get good and stable operation, it is also necessary to use process information in the form of a dynamic model between inputs and outputs both in the controller and in the design of the control architecture.

To help fulfill future energy demands, progress must be made in both the understanding and design of biomass conversion, and in the on-line control and management of such systems.

Some interesting questions are:

- What different type of models do we have to use for modeling of conversion processes?
- What are the advantages and drawbacks of these different types of models when we want to use the models for different applications?
- What are the basic functions to control when you want to convert biomass through thermal or biochemical/microbiological processes?
- What are the similarities and differences with respect to modeling aspects for the different types of conversion processes?

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CHAPTER 16

Energy and exergy analyses of power generation systems using biomass and coal co-firing

Marc A. Rosen, Bale V. Reddy & Shoaib Mehmood

16.1 INTRODUCTION

Coal-fired power plants are used worldwide for electricity production and provide over 42% of global electricity supply (International Energy Agency, 2010). However, emissions of greenhouse gases (CO_2 , CH_4 , etc.) from coal combustion systems are a major environmental concern. Among these gases, CO_2 is considered the most critical in terms of its contribution to global warming and coal-fired power plants account for 28% of global CO_2 emissions (International Energy Agency, 2010). Various methods have been developed to mitigate these emissions, with biomass co-firing with coal cited as one of the least expensive options (Basu *et al.*, 2011).

Biomass is a renewable energy source and considered as a CO_2 -neutral fuel since it releases no net CO_2 emissions if carefully managed. The use of biomass as a clean fuel has gained great interest in recent years. Biomass can be fired in dedicated boilers, but the combustion of biomass alone has many challenges (Demirbas, 2003). Due to lower heating value of biomass, the efficiency of biomass-based power plants is very low. Furthermore, the density of biomass fuels is lower and their particle size is higher than the corresponding values for coal. This means that a greater mass of biomass is required to produce the same amount of heat from the combustion as coal. Cost issues related to dealing with surplus biomass are another significant challenge. It is often technically and economically advantageous to use biomass as a supplemental fuel in existing coal-fired power plants.

Energy and exergy analyses are useful techniques for evaluating and optimizing the performance of energy-related systems or processes. Energy analysis, which is based on first law of thermodynamics, is the most commonly employed method for the analysis of the energy conversion processes. However, energy analysis does not account for energy quality and internal losses in processes. In contrast, exergy analysis is based on the second law of thermodynamics and identifies efficiencies that measure approach to ideality and the magnitude and locations of imperfections. This information can inform and drive efforts to improve the performance of systems and processes. Exergy analysis has been increasingly applied since 1960 (Ganapathy *et al.*, 2009).

Co-firing is a developing technology for which there is currently a great need for research. Many studies have been reported on biomass co-firing with coal. Experimental studies focus on evaluating the effects of co-firing on factors such as boiler performance, combustion characteristics, and gaseous and particulate emissions. However, there is a lack of studies related to energy and exergy analyses of coal co-firing with biomass in the open literature, and modeling studies on biomass co-firing with coal are also limited. This chapter seeks to address these needs and describes a simulation and analysis of a biomass co-firing based power generation system. Energy and exergy analyses are utilized to determine the impacts of biomass co-firing on system performance and gaseous emissions. The power generation system considered is a typical pulverized coal-fired steam cycle system, and four biomass fuels (rice husk, pine sawdust, chicken litter, and refuse derived fuel) and two coals (bituminous coal and lignite) are chosen for analysis.

This chapter begins with general information on biomass co-firing with coal. Then, a literature review of relevant studies and characteristics of the fuels are provided. The power plant utilized in

an analysis is then described, and assumptions and theory involved in thermodynamic modeling, simulation and analysis are presented. Finally, quantitative information on the use of biomass co-firing with coal, generated through simulations, is provided and discussed, and conclusions are drawn.

16.2 BACKGROUND

16.2.1 *Co-firing and its advantages*

Co-firing, also known as co-combustion, is the process of burning two types of fuel in the same boiler. Although many types of materials can be burned, the term co-firing usually refers to the combustion of solid biomass with coal in coal-fired boilers. In simple terms, biomass co-firing can be thought of as the process of partial supplementing of coal with biomass in coal-fired boilers.

Co-firing offers many advantages:

- Since co-firing is carried out in existing coal-fired plants, it can be implemented in a relatively short period of time and with a small investment.
- Biomass is CO₂ neutral, so biomass co-firing does not contribute to the greenhouse effect and can help reduce overall CO₂ emissions.
- Biomass fuels usually have less sulfur and less nitrogen than coal, so NO_x and SO_x emissions can in many cases be decreased by biomass co-firing.
- Co-firing biomass residues further mitigates greenhouse gas emissions by avoiding methane (CH₄) releases from the otherwise landfilled biomass (Demirbas, 2003; Sami *et al.*, 2001). This is significant because CH₄ is 21 times more potent as CO₂ in terms of global warming impact, and disposal of biomass residues is a major source of methane.
- Co-firing is an efficient way of biomass utilization in power generation. This is important because the actual efficiency of biomass power plants is generally in the range of 20 to 25%, which is much lower than for large coal units (Fanchi, 2004), and because biomass co-firing at a 3–5% ratio causes a decrease in boiler efficiency of less than 1% (Loo and Koppejan, 2008).
- Biomass co-firing offers flexibility in terms of fuel use, as the plant can still operate at 100% load with coal if no biomass is available.
- Biomass co-firing can provide companies with carbon or other credits in countries where government incentives are offered for displacing fossil fuels and using renewable energy and for mitigating carbon emissions.
- Communities located in the vicinity of the biomass co-firing plants can benefit economically from the production of biomass fuels.

16.2.2 *Global status of co-firing*

At present, biomass co-firing is considered as one of the fastest growing renewable technologies. It has become commercial in the US, Finland, Denmark, Germany, Belgium, The Netherlands, Poland, Austria, Spain, Australia, Japan, Great Britain and a number of other countries (Loo and Koppejan, 2008).

Currently there are over 228 co-firing installations worldwide (Al-Mansour and Zuwala, 2010). Continental Europe and the US are currently the leading regions with more than 100 and 40 plants, respectively (Fig. 16.1). Finland is the leading country with 78 plants, followed by the US, Germany, UK, Sweden, Denmark, Australia, Canada, Italy, The Netherlands, and Austria.

Co-firing has been practiced using a wide range of biomass fuels and all of the commercially significant solid fossil fuels. Co-firing has also been applied for many types of boilers, ranging in capacity from 50–700 MW_{el}, although a number of very small plants have also been used (Loo and Koppejan, 2008). Bubbling and circulating fluidized bed boilers and stoker boilers have been utilized, but most of the boilers involved in co-firing are pulverized coal boilers, including tangentially-fired, wall-fired, cyclone units.

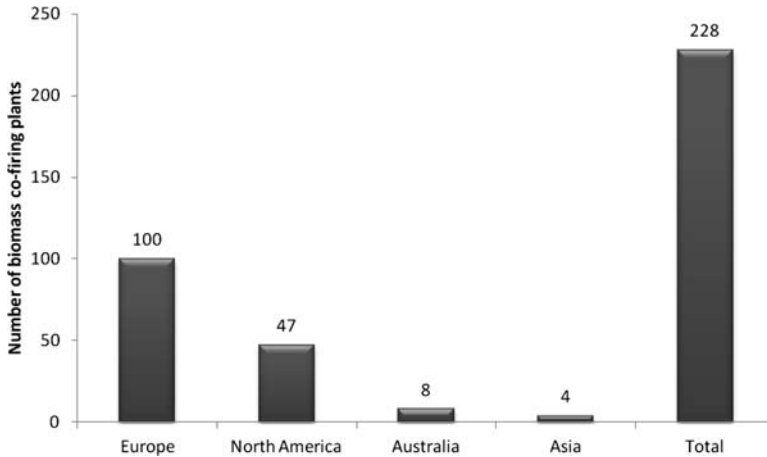


Figure 16.1. Worldwide distribution of biomass co-firing power plants (adapted from Al-Mansour and Zuwala, 2010).

Table 16.1. Selected properties of biomass fuels and coals. Adapted from Demirbas (2004).

Property	Biomass	Coal
<i>Thermophysical characteristics</i>		
Fuel density [kg/m^3]	~ 500	~ 1300
Particle size [mm]	~ 3	~ 0.1
Dry heating value [MJ/kg]	14–21	23–28
<i>Composition (wt% of dry ash)</i>		
SiO_2	23–49	40–60
K_2O	4–48	2–6
Fe_2O_3	1.5–8.5	8–18
Al_2O_3	2.4–9.5	15–25

16.2.3 Properties of biomass and coal

The properties of biomass and coal differ significantly, and these differences are important in incorporating biomass co-firing in coal-fired plants. Tables 16.1 and 16.2 compare the physical, chemical, and fuel properties of biomass fuels and coal, and highlight the following differences between biomass fuels and coals:

- In general, biomass is less dense than coal but the particle size of biomass is much higher than that of coal. Due to the larger particle size, biomass is more difficult to reduce to a small size. The large particle size of biomass fuels can also cause storage problems.
- Biomass has much less carbon, more oxygen and more moisture than coal, making the heating values of biomass fuels significantly lower than those of coals (Demirbas, 2002).
- The volatile matter of biomass fuels is significantly higher than that of coal and their fixed carbon/volatile ratios are much less than 1.
- Biomass fuels generally have less nitrogen and sulfur contents than coal, which are directly related to NO_x and SO_x emissions.
- Ash and nitrogen contents vary among biomass fuels. In general, woody biomass has less nitrogen and ash compared to agricultural materials. Ash content along with the high moisture

Table 16.2. Proximate and ultimate analyses [wt%] of biomass fuels and coals. Adapted from Vassilev *et al.* (2010).

Fuel	Proximate analysis (ar) ¹				Ultimate analysis (daf) ²					
	VM	FC	M	A	C	O	H	N	S	Cl
<i>Biomass fuels</i>										
Beech bark	67.5	17.0	8.4	7.1	51.4	41.8	6.0	0.7	0.11	0.11
Oak wood	73.0	20.0	6.5	0.3	50.6	42.9	6.1	0.3	0.10	—
Sawdust	55.1	9.3	34.9	0.7	49.8	43.7	6.0	0.5	0.02	0.01
Switch grass	70.8	12.8	11.9	4.5	49.7	43.4	6.1	0.7	0.11	0.08
Straw	64.3	13.8	12.4	9.5	48.8	44.5	5.6	1.0	0.13	0.54
Almond shell	69.5	20.2	7.2	3.1	50.3	42.5	6.2	1.0	0.05	0.06
<i>Coals</i>										
Lignite	32.8	25.7	10.5	31.0	64.0	23.7	5.5	1.0	5.8	0.01
Bituminous coal	33.4	34.1	8.2	24.3	74.4	17.7	5.6	1.4	0.9	0.03

¹As received basis.

²Dry ash free basis.

content of biomass can cause combustion and ignition problems. If the melting temperature of the dissolved ash is low, it can cause slagging and fouling (Sami *et al.*, 2001).

- Relative to coal, biomass has less aluminum, iron, silica, and titanium, but more potassium.
- Some biomass types, like straw and bark, contain relatively large amounts of chlorine. High chlorine and potassium concentrations can cause serious problems, such as slagging, fouling, and corrosion (Sami *et al.*, 2001). The major concern is high-temperature corrosion of superheater tubes induced by chlorine on the surface (Demirbas and Demirbas, 2003; Bryers, 1996).

16.2.4 Technology options for co-firing

There are currently three basic technology configurations for biomass co-firing with coal in power plants (Al-Mansour and Zuwala, 2010):

- Direct co-firing
- Parallel co-firing
- Indirect co-firing.

16.2.4.1 Direct co-firing

Direct co-firing (Fig. 16.2) involves the burning of biomass and coal in the same furnace. This is the most commonly applied and cheapest co-firing configuration. Many plants worldwide demonstrate this option. Examples of such plants are the Gelderland Power Station in the Netherlands (Loo and Koppejan, 2008) and the AES 108 MW_e tangentially-fired Greenidge Generation Station in Dresden, New York (International Energy Agency, 2009). Depending on the biomass fuel characteristics, the same or separate mills and burners can be used. The following four options are available for direct biomass co-firing in pulverized coal boilers:

- Biomass and coal are blended in the fuel handling system and then this blend is fed into the furnace. This is the most straightforward and least expensive option, but it can only be accomplished at low biomass percentages, usually <5% (Tillman, 2000), and only in conventional wall or corner-fired boilers (Maciejewska *et al.*, 2006). This option is also limited to some types of biomass fuels. Olive or palm kernels, cocoa shells and sawdust can be successfully co-fired with coal while herbaceous biomass causes many problems during feeding and sizing (Maciejewska *et al.*, 2006).
- This option involves the separate milling of biomass, but the pulverized biomass is injected into the existing pulverized coal pipe work either upstream of the burner or at the burners.

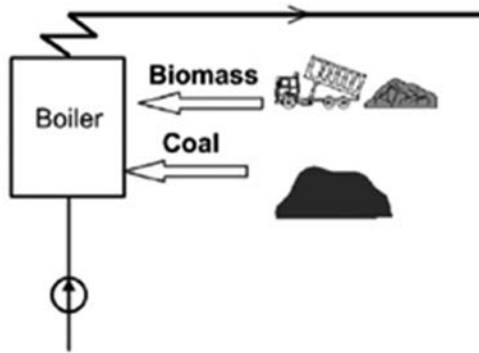


Figure 16.2. Layout of direct co-firing technology (adapted from Al-Mansour and Zuwala, 2010).

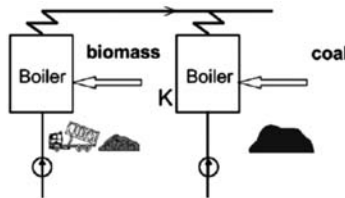


Figure 16.3. Layout of parallel co-firing technology (adapted from Al-Mansour and Zuwala, 2010). K represents coal-fired boiler.

This approach involves higher investment but co-firing at elevated ratios can be achieved (Loo and Koppejan, 2008; Maciejewska *et al.*, 2006).

- This option also involves separate biomass milling, but has two separate feeding lines. Coal utilizes the original injection system, whereas biomass is injected into the dedicated burners in the lower furnace. This approach is the most expensive of all direct co-firing options.
- Biomass is used as a reburn fuel to control NO_x emissions. Separate milling systems along with separate biomass-fired burners at the exit of the furnace are required in this approach.

16.2.4.2 Parallel co-firing

In this option, biomass is combusted in a separate boiler to produce low-grade steam for utilization in the coal-fired power plant (Fig. 16.3). The Avedore Unit 2 project in Copenhagen, Denmark is an example of this option (International Energy Agency, 2009). The investment in a parallel co-firing installation is higher than for direct co-firing, but it has the following advantages:

- The co-firing unit has no effect on the parent unit.
- Relatively difficult fuels with high alkali and chlorine contents can be used.
- Separate streams of biomass and coal ash are produced.

16.2.4.3 Indirect co-firing

In this type of co-firing, the solid biomass is gasified separately and the produced gas is combusted in the furnace of an existing coal-fired boiler (Fig. 16.4). The Unit 9 Amer power plant in the Netherlands is an example of indirect co-firing (International Energy Agency, 2009). Although this option has high investment costs, it offers the following advantages:

- A wide range of biomass fuels can be used since this type of co-firing requires no blending or mixing.
- Biomass ash is kept separate from coal ash.

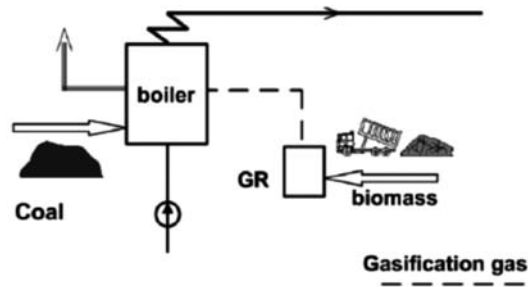


Figure 16.4. Layout of indirect co-firing technology (adapted from Al-Mansour and Zuwala, 2010). GR represents biomass gasifier.

- The risks of corrosion and fouling are low in this approach because, if the product gas contains impurities, e.g., alkali, chlorine, it can be cleaned before combustion in the furnace.
- The syngas is burnt above the burner, allowing for a reduction of NO_x emissions.

16.3 RELEVANT STUDIES ON CO-FIRING

16.3.1 Co-firing studies

In this section, general studies related to biomass co-firing in which researchers have summarized their experiences and reviewed the literature on co-firing, are summarized.

Demirbas (2003) comprehensively studies the co-firing of biomass with coal. This work includes a comparison of the physical, chemical, combustion, and ash properties of various biomass fuels with those of coal. He discusses fundamental differences in coal and biomass combustion, biomass combustion technologies, technology options for co-firing, and definitions related to co-firing, as well as mechanisms of co-firing, gasification, and pyrolysis.

Tillman (2000) reviews co-firing of biomass and coal, including a brief description of technology options for co-firing and a summary of his experiences at various co-firing based power plants in the US. The influence of co-firing on the combustion process, gaseous emissions, and boiler efficiency is documented for many power plants.

Sami *et al.* (2001) review the literature on co-firing of coal with biomass. Basic concepts related to coal and biomass combustion, and technology options for co-firing, is discussed. Results from various experimental and numerical studies of co-firing are presented, and issues related to co-firing of coal with biomass identified.

Savolainen (2003) describes his experiences at the Naantali Power Plant where co-firing tests of coal with sawdust were performed to investigate the impact of co-firing on boiler performance, flame stability, and emissions.

Baxter (2005) comprehensively investigates technical boiler issues associated with co-firing, the main ones of which include fuel supply, handling, and storage, ash deposition, fuel conversion, pollutant formation, corrosion, fly ash utilization, impacts on selective catalytic reduction (SCR) systems, and the formation of strained flows. Possible measures for managing corrosion, fly ash utilization, formation of strained flows, and impacts on SCR systems are discussed.

A review of biomass co-firing experiences worldwide was recently reported by Al-Mansour and Zuwala (2010), including descriptions of the current status of co-firing power plants and current/available co-firing technologies worldwide, and key parameters to evaluate biomass co-firing technologies. Implemented co-firing technologies in Europe are assessed to show that indirect co-firing is the most advantageous technology followed by direct co-firing in pulverized fuel, bubbling fluidized boiler, and circulating fluidized bed boilers.

16.3.2 Experimental studies

The majority of the experimental studies related to biomass co-firing are limited to studying its impact on gaseous emissions and boiler operation, although some investigate flame stability, particulate matter emissions, and combustion characteristics.

Spilthoff and Hein (1998) experimentally study the effects of coal co-combustion with straw, miscanthus, wood and municipal sewage sludge on SO_x and NO_x emissions. The results demonstrate that SO_x emissions decrease for straw, miscanthus, and wood as these fuels have less sulfur content than coal. But municipal sewage sludge co-firing increases SO_x emissions due to its higher sulfur content than coal. NO_x emissions depend on the raw fuel content and can be reduced by air staging and fuel reburning.

Gani *et al.* (2005) experimentally investigate an electrically heated tube furnace to determine the effects of co-combustion of coal/coal mixtures with biomass on ignition behavior, combustion efficiency, NO_x emissions, and size of ash particles. The results show that biomass enhances the ignition behavior of low rank coals during co-firing, due to the high volatile matter content of biomass. The concentrations of NO and N_2O during co-combustion remain the same as during coal combustion alone, but co-combustion shifts particle size distributions from fine to coarse.

Kruczek *et al.* (2006) conduct a series of experiments on a laboratory scale isothermal flow reactor by varying fuel type, particle size, combustion temperature, and excess air ratio. They show that biomass addition enhances the combustion process. An increase in biomass proportion in the mixture reduces NO_x and SO_x emissions.

Kwong *et al.* (2007) investigate experimentally the effects of co-combustion on combustion temperature and gaseous emissions of CO_2 , CO, NO_x , and SO_x . They observe that the combustion temperature and all gaseous emissions decrease with increased biomass blending ratio in the mixture. An important result is that biomass-grinding size has no obvious effect on combustion temperature and gaseous emissions, although relative moisture content appears to affect these parameters. Higher moisture content in the mixture causes a reduction in the combustion temperature, resulting in a higher unburned fraction and leading to a decrease in CO_2 and NO_x emissions and an increase in SO_x and CO emissions.

Chao *et al.* (2008) evaluate the effects of coal co-firing with rice husk and bamboo on particulate matter and associated polycyclic aromatic hydrocarbon (PAH) emissions. Combustion performance of the system is observed to improve during co-firing, due to the higher volatile matter content of biomass, which shortens the combustion time scale. As a result, particulate matter and PAH emissions are reduced during co-firing. Enlarged grinding size of biomass is observed not to affect combustion performance significantly.

Demirbas (2008) experimentally examines the co-firing of municipal solid waste (MSW) and coal in a bench-scale bubbling fluidized bed combustor. This work includes a discussion of the differences in fundamental properties and ash properties of coal and MSW, and the effects of co-firing MSW with coal on gaseous emissions.

Lawrence *et al.* (2009) experimentally study coal co-firing with dairy biomass in a small-scale 29 kW_t furnace. The effect of co-firing on combustion and NO_x emissions is evaluated, showing that a blend of dairy biomass and coal burned more completely than coal alone due to the earlier release of biomass volatiles than those of coal. In addition, NO_x emissions are found to increase in lean mixtures, but a very low reduction is observed in rich mixtures due to a lower fraction of fuel bound nitrogen being available to convert to NO_x .

16.3.3 Modeling and simulation studies

There is a dearth of simulation studies related to biomass co-firing with coal. Abbas *et al.* (1994) developed a numerical model for sawdust co-firing with coal in a 0.5 MW pulverized coal boiler. They utilize the turbulence decay model for volatile combustion, diffusive radiation model, and k - ϵ model to develop the code and investigate the influence of burned injection mode on burnout and NO emissions.

Backreedy *et al.* (2005) model the co-firing of pulverized coal and pinewood in a 1 MW combustor using a commercially available computational fluid dynamics (CFD) code (Fluent version 6). They investigate the impact of biomass particle size and shape on the burnout of blended char.

Huang *et al.* (2006) use the ECLIPSE process simulator on a pressurized fluidized bed combustion (PFBC) combined cycle power plant to examine the impact of coal co-firing ratio of biomass on energy efficiency, plant equipment, and gaseous emissions. They selected an American Federal coal of medium calorific value, and five types of biomass fuel (willow chips, straw, switch grass, miscanthus, and olive pits). They observe that the gas turbine output increases while that of the steam turbine decreases with an increase in co-firing ratio. For all types of biomass, the net CO₂ and SO_x emissions are found to decline as the amount of biomass in the blend increases. On the contrary, NO_x increases, except for willow chips because it has the lowest nitrogen content. With increasing co-firing ratio, the overall plant efficiency decreases, with the lowest value found for willow chips due to its having the highest moisture content among the selected biomass fuels.

Doshi *et al.* (2009) mathematically model the ash formation behavior during co-firing to allow the prediction of the ash transformation and formation behavior during co-firing of biomass and coal.

Ghenai and Janajreh (2010) apply computational fluid dynamics (CFD) to a co-pulverized coal/wheat straw furnace to investigate the effects of co-firing on flow field, gas and particle temperature distributions, particle trajectories, and gas emissions.

16.3.4 Energy and exergy analyses

Few energy and exergy studies of biomass co-firing with coal are reported in the literature. Zuwala and Sciazko (2010) perform an energy analysis of a tangentially-fired co-pulverized boiler. The experimental results show that co-firing of coal and bio-waste consisting of biomass with a mass share of 6.6% or sawdust with a mass share of 9.5% has no adverse effect on boiler efficiency. However, slagging and fouling conditions worsen as a result of co-firing instead using coal alone. The calculated emission indices show that biomass co-firing reduces CO₂ and SO₂ emissions. Martin *et al.* (2006) perform an exergy analysis of atmospheric bubbling fluidized bed co-combustion of low-grade coal mixtures with pine chips. Exergy efficiencies and irreversibilities are calculated for nine experiments to identify the sources of exergy destruction. The performance of the plant is found to be improvable by decreasing the exit temperature of the exhaust gas.

16.3.5 Economic studies

Economic analyses of co-firing plant are limited. De and Assadi (2009) develop a techno-economic model to investigate the economics of biomass co-firing. The model is based on pilot plant test results. The total additional cost as well as additional specific costs can be estimated with the model. The model can also assess the economic feasibility of retrofitting for biomass co-firing and estimate the required incentives for this purpose.

Basu *et al.* (2011) perform an economic analysis of an existing 150 MW pulverized coal-fired power plant in Eastern Canada by considering three co-firing options (direct, indirect, gasification based). Capital and operating costs are calculated to determine the internal rate of return (IRR). The CO₂ reduction cost is also computed for the three options and compared with CO₂ sequestration costs.

16.4 CHARACTERISTICS OF BIOMASS FUELS AND COALS

Four biomass fuels (rice husk, pine sawdust, chicken litter, and refuse derived fuel) and two coals (bituminous coal and lignite) are considered in this chapter, and its simulations and assessments.

Table 16.3. Characteristics of selected solid fuels.

Parameter	Chicken litter ¹	Pine Sawdust ¹	Refuse derived fuel ¹	Rice husk ²	Bituminous coal ³	Lignite ³
Proximate analysis [wt%, as received]						
Fixed carbon	13.1	14.2	0.5	20.1	53.9	35.0
Volatile matter	43.0	70.4	70.3	55.6	28.2	44.5
Moisture	9.3	15.3	4.2	10.3	7.8	12.4
Ash	34.3	0.1	25.0	14.0	10.1	8.1
Ultimate analysis [wt%, as received]						
Hydrogen	3.8	5.0	5.5	4.5	3.9	4.1
Carbon	34.1	43.2	38.1	38.0	70.3	51.0
Oxygen	14.4	36.3	26.1	32.4	6.4	23.8
Nitrogen	3.50	0.08	0.78	0.69	1.07	0.4
Sulfur	0.67	—	0.33	0.06	0.41	0.16
Ash analysis [wt%]						
SiO ₂	5.77	9.71	38.67	94.48	51.67	46.15
Al ₂ O ₃	1.01	2.34	14.54	0.24	29.15	20.91
Fe ₂ O ₃	0.45	0.10	6.26	0.22	10.73	6.77
CaO	56.85	46.88	26.81	0.97	3.72	12.54
SO ₃	3.59	2.22	3.01	0.92	1.47	8.00
MgO	4.11	13.80	6.45	0.19	1.41	2.35
K ₂ O	12.19	14.38	0.23	2.29	0.29	1.49
TiO ₂	0.03	0.14	1.90	0.02	1.24	0.77
Na ₂ O	0.60	0.35	1.36	0.16	0.31	0.73
P ₂ O ₅	15.40	6.08	0.77	0.54	—	0.29
Heating value [kJ/kg] ⁴						
Higher heating value	14240	17280	16620	14980	28330	20070
Lower heating value	13410	16180	15410	13990	27340	19070

¹Vassilev *et al.* (2010).²Madhiyanon *et al.* (2009).³Vassilev and Vassileva (2007).⁴Calculated from equations (16.1)–(16.3).

Each biomass is selected from a different biomass classification. Similarly, the coals considered are from two different classes. Table 16.3 lists the basic information about the feedstocks utilized in the simulations.

The higher heating value (*HHV*) of biomass can be expressed as follows (Loo and Koppejan, 2008):

$$HHV_b = 0.3491C_b + 1.1783H_b + 1.005S_b + 0.0151N_b - 0.1034O_b - 0.0211A_b \quad (16.1)$$

where subscript *b* denotes biomass, and C, H, S, N, O, and A denote carbon, hydrogen, sulfur, nitrogen, oxygen, and ash contents of biomass in weight%. The lower heating value (*LHV*) of coal can be expressed as follows (Ghamarian *et al.*, 1982):

$$LHV_c = 427.0382n_C + 90.88110n_H - 207.46424n_O + 297.0116n_S \quad (16.2)$$

where subscript *c* denotes coal, *n* is the number of moles of a constituent, and other terms are as defined earlier. For a given substance, the higher and lower heating values related:

$$HHV = LHV + 21.978n_H \quad (16.3)$$

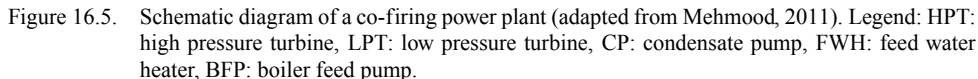


Figure 16.5 presents a schematic of a co-firing based power plant. The configuration employed is of the direct co-firing type, which is the most commonly applied co-firing configuration. Pulverized biomass mixes with pulverized coal in the fuel transport lines just before the burners because co-firing at elevated ratios can be achieved by this type of mixing (section 16.2.4.1). Both air and the fuels enter the boiler at the environment temperature and pressure. Combustion occurs in the combustion chamber and the flue gases exit through the stack after exchanging the heat with the feed water. Superheated steam from the super heater enters the high-pressure turbine. Some of the steam is extracted from the turbine after partial expansion and routed to the open feed water heater while the remaining steam is reheated after expansion to the original temperature. It then expands through the low pressure turbine to the condenser pressure. The reheater pressure is 25% of the original pressure. Steam and condensate exit the feed water heater as a saturated liquid at the extraction pressure. The condensate leaving the condenser mixes with the feed water exiting the feed water heater and is then pressurized in the pump to the boiler pressure.

The co-firing configuration in Figure 16.5 is used for the simulations and analyses presented in this chapter. Flow data for all the components for both base coals (100% coal) are listed in Tables 16.4 and 16.5.

Table 16.4. Flow data for coal-fired power plant using 100% bituminous coal.

Stream	Mass flow rate [kg/s]	Temperature [°C]	Pressure [bar]	Energy rate [MW]	Exergy rate [MW]
1	1	8	1.013	28.33	29.27
2	2.31	8	1.013	0.00	0.046
3	0.002	600	1.013	0.01	0.001
4	11.87	1886	1.013	26.22	20.96
5	11.87	150	1.013	2.867	2.47
6 ¹	0.08	150	1.013	0.009	0.01
7	8.44	600	120	30.46	29.33
8	8.44	395.9	30	27.20	26.07
9	2.35	395.9	30	7.57	7.22
10	6.09	600	30	22.44	21.60
11	6.09	36.17	0.06	15.35	14.50
12	6.09	36.17	0.06	0.92	0.14
13	6.09	36.35	3	0.94	0.16
14	8.44	233.9	3	8.51	7.41
15	8.44	236.2	120	8.62	7.52
16	596.4	8	1.013	20.10	0.00
17	596.4	16	1.013	40.07	19.52

¹Flow 6 is not shown in Figure 16.8 but represents fly ash carried with flue gases through the stack.
Adapted from Mehmood (2011).

Table 16.5. Flow data for coal-fired power plant using 100% lignite.

Stream	Mass flow rate [kg/s]	Temperature [°C]	Pressure [bar]	Energy rate [MW]	Exergy rate [MW]
1	1	8	1.013	20.07	21.19
2	2.31	8	1.013	0.00	0.031
3	0.001	600	1.013	0.009	0.001
4	8.40	1734	1.013	18.12	14.59
5	8.40	150	1.013	3.086	2.24
6	0.06	150	1.013	0.007	0.014
7	5.82	600	120	21.00	20.21
8	5.82	395.9	30	18.75	17.96
9	1.62	395.9	30	5.22	4.96
10	4.24	600	30	15.47	14.88
11	4.24	36.17	0.06	10.58	9.80
12	4.24	36.17	0.06	0.64	0.10
13	4.24	36.35	3	0.65	0.11
14	5.82	233.9	3	5.87	5.11
15	5.82	236.2	120	5.94	5.18
16	411.3	8	1.013	13.86	0.00
17	411.3	16	1.013	27.63	13.46

Adapted from Mehmood (2011).

16.6 THERMODYNAMIC MODELING, SIMULATION AND ANALYSIS OF CO-FIRING SYSTEMS

16.6.1 Approach and methodology

In this section, we describe the modeling, simulation and analysis of the performance of and emissions of co-firing system. Energy and exergy balances are developed for the overall system

and its components. A model is generated using the balances and assumptions, and utilized to investigate the system performance and emissions by varying input conditions.

In the analyses, the operating temperatures and pressures of the components of the steam cycle are held fixed while the feed rate to the boiler is changed by varying fuel type and co-firing ratio. To determine the effect of biomass addition in the blend, the boiler is first fed with coal alone and the system performance and emissions are analyzed. Then, the boiler is fed with biomass and coal in a co-firing mode and system performance and emissions are compared with that of coal firing alone for different co-firing conditions and different fuel types.

Two cases of boiler feed conditions are considered. In both cases, the mass flow rate of coal at one particular co-firing condition remains constant for all combinations of fuels. The first case involves a fixed fuel flow rate and parameters are evaluated on the basis of a unit fuel flow rate. The mass flow rate of coal is decreased from 1 kg/s to 0.75 kg/s in intervals of 0.05 kg/s, while that of biomass is increased from 0 kg/s to 0.30 kg/s. In the second case, heat input to the steam cycle is held fixed at that produced by the burning 1 kg/s of coal alone in the boiler. In this case, the mass flow rate of coal is decreased from 1 kg/s to 0.75 kg/s in intervals of 0.05 kg/s and the additional amount of biomass fuel required to maintain the fixed heat to the boiler is found. The operating temperatures and pressures of all steam cycle components remain unchanged at all co-firing conditions, for both cases. In the second case, the steam flow rate in the cycle also remains constant. However, in the first case, due to the changing fuel feed rate to the boiler, the mass flow rate of the steam varies at different co-firing conditions which consequently changes the energy flows at the inlet and outlet of the components. Thus, the network output of the plant also changes at with co-firing ratio for the first case.

16.6.2 Assumptions and data

Typical values for parameters in the simulations and analyses are used, based on ranges reported in the literature. These values and the assumptions utilized to simplify the assessments are as follows:

- All system components operate at steady state conditions.
- All gases behave ideally.
- Kinetic and potential energy effects are minor and thus neglected.
- Ambient air is taken to be composed of 79% nitrogen and 21% oxygen on a volume basis.
- 20% excess air is provided to the combustor, based on typical values recommended for pulverized boilers (Basu *et al.*, 2000; de Souza-Santos, 2010).
- The ambient conditions are 8°C and 1.013 bar, respectively, and these are taken to be the temperature and pressure of the reference environment.
- 80% of the ash in the combusted fuel is assumed to be fly ash, while the remaining 20% is collected as bottom ash (Drably *et al.*, 1996), and the ash is inert.
- The bottom ash temperature is set at 600°C, based on an observed value for pulverized boilers with dry bottoms (Basu *et al.*, 2000).
- Combustion is taken to be complete all carbon in the fuel is converted to CO₂. This assumption is based on reports that there are no incomplete combustion losses for pulverized coal boilers (Basu *et al.*, 2000), and because the addition of biomass to coal enhances the combustion characteristics of the fuel because of the high volatile content of biomass.
- All sulfur in the fuel is oxidized to SO₂. In reality, SO_x emissions are due to formation of sulfur dioxide (SO₂) and sulfur trioxide (SO₃), but SO₃ typically constitutes around 10% of SO_x emissions (Bellhouse and Whittington, 1996). Since both biomass and coal contain small amounts of sulfur, quantities of SO₃ are produced are very small.
- NO_x emissions from combustion are in the form of nitric oxide (NO) and nitrogen dioxide (NO₂), and 96% of NO_x emissions are taken to be associated with NO formation and 4% with NO₂ formation based on reported values (Bellhouse and Whittington, 1996; Sarofim and Flagan, 1976; Phong-Anant *et al.*, 1985; Miller and Bowman, 1989).

- The formation of NO takes place through three paths: fuel bound nitrogen conversion, thermal fixation of atmospheric nitrogen at elevated temperatures (typically above 1500°C), and prompt formation resulting from rapid reactions in the flame zone involving nitrogen and fuel bound hydrocarbon radicals. Of the total NO formed, the contributions from fuel, thermal and prompt paths are taken to be 80, 16 and 4%, respectively, based on typical reported values (Bellhouse and Whittington, 1996; Phong-Anant *et al.*, 1985).
- 30% of the fuel nitrogen is converted to NO, based on observations (Bellhouse and Whittington, 1996; Phong-Anant *et al.*, 1985).
- Radiation and convective heat losses from the boilers and unburned fuel losses due to the presence of combustibles in the ash are each taken to be 1.5% of the fuel energy input, based on typical values for large boilers (Basu *et al.*, 2000; de Souza-Santos, 2010).
- Flue gases exit the stack at 150°C (Basu *et al.*, 2000).
- All components of the steam cycle are adiabatic, except where heat transfers occur.
- The isentropic and mechanical efficiencies of all steam turbines are 85% and 99%, respectively, the isentropic efficiency of all pumps is 88%, and the generator efficiency is 98%, based on typical values (Drbl *et al.*, 1996; Suresh *et al.*, 2010; Aljundi, 2009).

16.6.3 Governing equations

Mass, energy and exergy balances are used to determine the inputs and outputs, energy and exergy efficiencies, and irreversibilities. For a steady state process, general balances for mass, energy, and exergy can be written as (Moran and Shapiro, 2007; Dincer and Rosen, 2013):

$$\sum_i \dot{m}_i = \sum_e \dot{m}_e \quad (16.4)$$

$$\sum_i \dot{m}_i h_i + \dot{Q} = \sum_e \dot{m}_e h_e + \dot{W} \quad (16.5)$$

$$\sum_i \dot{E}x_i + \sum_j \left[1 - \frac{T_o}{T_j} \right] \dot{Q}_j = \sum_e \dot{E}x_e + \dot{W} + \dot{I} \quad (16.6)$$

The exergy associated with a flow of matter is the sum of its physical and chemical exergy. Both physical and chemical exergy terms are considered for the boiler because chemical reaction occur in the combustion chamber, while only physical exergy is considered in the steam cycle components. The specific physical exergy is defined as:

$$ex^{ph} = (h - h_o) - T_o(s - s_o) \quad (16.7)$$

Similarly, the specific chemical exergy for an ideal gas mixture can be written as:

$$ex^{ch} = ex_o^{ch} + R_u T_o \ln x_i \quad (16.8)$$

where x_i , ex_o^{ch} , and R_u denote respectively the mole fraction of species i , the molar exergy at the reference temperature, and the universal gas constant. Values for the standard molar exergy and standard molar enthalpy for various substances are listed in Table 16.6, based on the model of Morris and Szargut (1986). The molar exergy at the reference temperature can be expressed as follows (Kotas, 1980):

$$ex_o^{ch} = \frac{T_o}{T^o} ex_o^{ch} - \frac{\bar{h}_f^o(T^o - T_o)}{T^o} \quad (16.9)$$

where ex_o^{ch} , $\bar{h}_f^o$, T^o , and T_o denote respectively the standard molar chemical exergy, the standard enthalpy of formation, the standard temperature, and the reference temperature.

Table 16.6. Standard enthalpy and exergy values of selected substances.

Substance	Standard enthalpy [MJ/mol]	Standard exergy [MJ/mol]
O ₂ (g)	0	3.97
N ₂ (g)	0	0.72
CO ₂ (g)	−393.52	19.87
H ₂ O (g)	−241.82	9.5
H ₂ O (l)	−285.83	0.9
SO ₂ (g)	−297.10 ¹	313.40
NO (g)	90.59 ¹	88.90
NO ₂ (g)	33.72 ¹	55.60

¹Values for these constituents have been taken from Engineering Equation Solver.
Source: Moran and Shapiro (2007).

16.6.3.1 Analysis of boiler

The boiler is divided into two subsystems: combustor and heat exchangers (superheater and reheater). Mass, energy and exergy balances are written for each of these subsystems.

For a steady state reacting process involving no work, the energy and exergy balances for the combustor reduce to:

$$\sum_i \dot{n}_R \bar{h}_R + \dot{Q}_{Heat} = \sum_e \dot{n}_P \bar{h}_P \quad (16.10)$$

$$\sum_i \dot{E}x_R + \dot{E}x_{Heat} = \sum_e \dot{E}x_P + \dot{I}_{cc} \quad (16.11)$$

In equations (16.10) and (16.11), $\dot{n}_R, \dot{n}_P, \bar{h}_R, \bar{h}_P, \dot{Q}_{Heat}, \dot{E}x_R, \dot{E}x_P, \dot{I}_{cc}$, and $\dot{E}x_{Heat}$ denote respectively the molar flow rate of reactants, molar flow rate of products, molar specific enthalpy of reactants, molar specific enthalpy of products, heat loss from the combustor or boiler, exergy flow rate of fuel, exergy flow rate of air, exergy flow rate of hot products, irreversibility rate of combustion chamber, and exergy loss rate due to radiation and convective from the exterior surface of the furnace.

The molar flow rate of the reactants is the sum of molar flow rates of carbon, hydrogen, oxygen, sulfur, ash, moisture, and air. The flow rate of all reactants, excluding air, is found from the ultimate analysis as:

$$a_1 = \frac{P_c C_c + P_b C_b}{M_C} \quad (16.12)$$

$$a_2 = \frac{P_c H_c + P_b H_b}{M_H} \quad (16.13)$$

$$a_3 = \frac{P_c O_c + P_b O_b}{M_O} \quad (16.14)$$

$$a_4 = \frac{P_c N_c + P_b N_b}{M_N} \quad (16.15)$$

$$a_5 = \frac{P_c S_c + P_b S_b}{M_S} \quad (16.16)$$

$$a_6 = \frac{P_c w_c + P_b w_b}{M_w} \quad (16.17)$$

where a_1 to a_6 are the molar flow rate of carbon, hydrogen, oxygen, nitrogen, sulfur, and moisture, respectively. The subscripts c and b denote coal and biomass, while the letters P and M represent the percent share of co-firing and molecular weight, respectively.

For convenience, the calculations for the ash are done on a mass basis. The mass flow rate of ash is expressible as:

$$\dot{m}_{ash} = P_c \dot{m}_{ash,c} + P_b \dot{m}_{ash,b} \quad (16.18)$$

The molar specific enthalpy of a compound at a state other than the standard state is the sum of the enthalpy of formation of the compound and the specific enthalpy change between the standard state and the actual state. That is:

$$\bar{h}(T, p) = \bar{h}_f^\circ + \bar{h}(T, p) - \bar{h}_o \quad (16.19)$$

The enthalpies of formation for several compounds used in the analysis at various temperatures are included in the Engineering Equation Solver database. However, the enthalpy of formation of both coal and biomass are found as (Eisermann *et al.*, 1980):

$$\bar{h}_{fuel}^\circ = \overline{HHV}_{fuel} + a_1 \bar{h}_{CO_2}^\circ + \frac{a_2}{2} \bar{h}_{H_2O}^\circ + a_5 \bar{h}_{SO_2}^\circ \quad (16.20)$$

where $\bar{h}_{CO_2}^\circ$, $\bar{h}_{H_2O}^\circ$, and $\bar{h}_{SO_2}^\circ$ denote the standard enthalpies of formation of carbon dioxide, moisture, and sulfur dioxide, respectively, a_1 , a_2 , and a_5 are as previously defined. The higher heating value of fuel ($\overline{HHV}_{fuel}$) can be written as:

$$\overline{HHV}_{fuel} = P_c \overline{HHV}_c + P_b \overline{HHV}_b \quad (16.21)$$

The change in enthalpy of the fuel as:

$$\Delta h_{fuel} = C_{p,fuel} (T_o - T^o) \quad (16.22)$$

and the specific heat of the fuel ($C_{p,fuel}$) as:

$$C_{p,fuel} = FC_F + V_1 C_{V_1} + V_2 C_{V_2} \quad (16.23)$$

Here, F , V_1 , and V_2 denote respectively the mass fractions of fixed carbon, primary volatile matter, secondary volatile matter, and C_F , C_{V_1} and C_{V_2} denote respectively the specific heats of fixed carbon, primary volatile matter, and secondary volatile matter on a dry ash-free basis. Fixed carbon is taken from proximate analysis of the fuel. Primary volatile matter is taken to be the amount in excess of 10% on a dry, ash free basis. The secondary volatile matter is taken to be 10% if the total volatile matter content is greater than 10%. Temperature-dependent expressions for the specific heats of fixed carbon, primary volatile matter, and secondary volatile matter can be written as:

$$C_F = -0.218 + 3.807 \times 10^{-3} T - 1.7558 \times 10^{-3} T^2 \quad (16.24)$$

$$C_{V_1} = 0.728 + 3.391 \times 10^{-3} T \quad (16.25)$$

$$C_{V_2} = 2.273 + 2.554 \times 10^{-3} T \quad (16.26)$$

The specific heat of fuel in equation (16.23) is on a dry, ash-free basis. To determine the specific heat on an as-received basis, the specific heats of ash and moisture are summed in equation (16.23).

The specific heat of ash can be determined by summing the products of the weight percent and specific heat for each of the individual components. The specific heat for the constituents of the ash can be expressed as follows (Berman and Brown, 1985):

$$C_{pac} = K_o + K_1 T^{-0.5} + K_2 T^{-2} + K_3 T^{-3} \quad (16.27)$$

Values for the coefficients K_0 , K_1 , K_2 , and K_3 for all constituents of ash except SO_3 and P_2O_5 are listed in Table 16.7. The specific heats of SO_3 and P_2O_5 are taken from NIST standard reference data (National Institute of Standards and Technology, 1965). Moreover, temperature is in Kelvin.

Table 16.7. Coefficients for correlation for specific heat of ash [kJ/kmol].

Constituent	K	$K_1 \times 10^{-2}$	$K_2 \times 10^{-5}$	$K_3 \times 10^{-7}$
SiO ₂	80.01	-2.403	-35.47	49.16
Al ₂ O ₃	155.02	-8.28	-38.61	40.91
Fe ₂ O ₃	146.86	0	-55.77	52.56
CaO	58.79	-1.34	-11.47	10.30
MgO	58.179	-1.61	-14.05	11.27
TiO ₂	77.84	0	-33.68	40.29
Na ₂ O	95.148	0	-51.04	83.36
K ₂ O	105.40	-5.77	0	0

Source: Berman and Brown (1985).

As both fuel and air enter the combustion chamber at ambient conditions, their physical exergies are both zero. However, the specific chemical exergy of fuel can be expressed as (Szargut, 2005):

$$ex_f^{ch} = \beta_f(LHV_f + wh_{fg}) + wex_{water,o}^{ch} \quad (16.28)$$

where LHV_f , w , h_{fg} , and $ex_{water,o}^{ch}$ denote respectively the lower heating value of fuel, the weight percent of moisture in the fuel, the enthalpy of evaporation of water, and the specific chemical exergy of liquid water at the reference conditions. The coefficient β_f is developed from statistical correlations and the relations for coal and biomass are:

$$\beta_c = 1.0437 + 0.1869(H/C) + 0.0617(O/C) + 0.0428(N/C) \quad (16.29)$$

$$\beta_b = \frac{1.044 + 0.0160(H/C) - 0.3493(O/C)\{1 + 0.0531(H/C)\}}{1 - 0.4124(O/C)} \quad (16.30)$$

where C, H, O, and N denote respectively the weight percents of the carbon, hydrogen, oxygen, and nitrogen in the fuel, and are obtained from the ultimate analysis.

The chemical exergy rate of the air is calculated with equation (16.8) as:

$$\dot{E}x_{air}^{ch} = A_a[\epsilon_{O_{2,o}}^{ch} + 3.76 \epsilon_{N_{2,o}}^o + R_u T_o \{\ln(0.21) + \ln(0.79)\}] \quad (16.31)$$

After combustion, the hot products leave the furnace at T_p . 80% of the ash in fuel being fired exits with flue gases, while the remainder is collected as bottom ash. Energy losses due to unburned combustibles in the ash and radiation and convective heat losses through the boilers are each taken to be 1.5% of fuel energy input. The external wall temperature of the furnace is required to determine the thermal exergy loss rate from the exterior surface of boiler, and can be evaluated with the following empirical relationship (de Souza-Santos, 2010), which was developed by Isachenko and colleagues:

$$U[T_{ow} - T_o] = \frac{k_{ins}(T_f - T_{ow})}{X_{ins}} \quad (16.32)$$

where U , k_{ins} , X_{ins} , T_f , and T_{ow} denote respectively the overall heat transfer coefficient, the thermal conductivity of the wall insulation material, the insulation thickness, the furnace temperature, and the wall temperature. The insulation thermal conductivity and thickness are assumed to be 0.06 W/m K and 5 mm, respectively. The overall heat transfer coefficient can be written as:

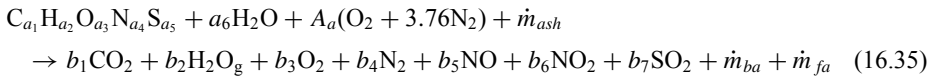
$$U = 1.9468[T_{ow} - T_o]^{1/4}(2.68633V + 1)^{1/2} + 5.75 \times 10^{-8} \epsilon_{ins} \frac{T_{ow}^4 - T_o^4}{T_{ow} - T_o} \quad (16.33)$$

Here, V and ε_{ins} are the wind velocity and insulation emissivity, respectively. The average wind velocity for Toronto (4 m/s or 9 mph) and a typical insulation emissivity (0.01) are used here. An empirical formula suggested originally by Blokh, can be used to estimate the furnace temperature (Basu *et al.*, 2000):

$$T_f = 0.925\sqrt{T_{ad} \times T_p} \quad (16.34)$$

Here, T_{ad} and T_p are the adiabatic flame temperature and furnace gas exit temperature, respectively.

The molar flow rate of the products and the excess air can be found from the combustion equation. The following general chemical reaction, accounting for reactants entering and products leaving the combustion chamber, can be written:



Here, b_1 to b_6 are molar flow rates of the respective flue gases, while A_a , $\dot{m}_{ba}$, and $\dot{m}_{fa}$ are the molar flow rate of air, the mass flow rate of bottom ash, and the mass flow rate of fly ash, respectively. Balances for each element in the reactants and products yield following relations:

Carbon balance:

$$b_1 = a_1 \quad (16.36)$$

Hydrogen balance:

$$b_2 + a_6 = 2b_2 \quad (16.37)$$

Oxygen balance:

$$a_3 + a_6 + 2A_a = 2b_1 + b_2 + 2b_3 + b_5 + 2b_6 + 2b_7 \quad (16.38)$$

Nitrogen balance:

$$a_4 + 7.52A_a = 2b_4 + b_5 + b_6 \quad (16.39)$$

Here, the second term on the right hand side (b_5) denotes the molar flow rate of nitrogen oxide (NO), for which a balance can be written using the assumptions in section 16.5.1 as:

$$b_5 = 0.3a_4 + 3.76\alpha A_a + \beta \quad (16.40)$$

where the first, second, and third (β) terms on the right hand side represent the formation of nitrogen oxide through fuel-bound nitrogen, thermal, and prompt paths, respectively. Since 30% of fuel nitrogen is assumed converted to nitrogen oxide, a_4 is multiplied by 0.3. The balances for thermal and prompt NO are:

$$3.76\alpha A_a = 0.16b_5 \quad (16.41)$$

$$\beta = 0.04b_5 \quad (16.42)$$

In equation (16.39), b_6 is the molar rate of NO_2 , for which a balance can be written as:

$$b_6 = 0.04(b_5 + b_6) \quad (16.43)$$

sulfur balance:

$$a_5 = b_7 \quad (16.44)$$

ash balance:

$$\dot{m}_{ash} = 0.2\dot{m}_{ba} + 0.8\dot{m}_{fa} \quad (16.45)$$

The molar specific enthalpy of flue gases can be determined with equation (16.19). The chemical exergy and physical exergy for the flue gases can be determined with equations (16.8) and

Table 16.8. Molecular weight, standard enthalpy, and standard entropy of ash constituents.

Constituent	Molecular weight [kg/kmol]	Standard enthalpy [MJ/kmol]	Standard entropy [kJ/kmol · K]
Silica (SiO ₂)	60	−911.3	41.9
Aluminum oxide (Al ₂ O ₃)	102	−1674.4	51.1
Ferric oxide (Fe ₂ O ₃)	160	−825.9	90.0
Calcium oxide (CaO)	56	−634.6	39.8
Magnesium oxide (MgO)	40	−601.5	26.8
Titanium oxide (TiO ₂)	80	−945.2	50.2
Alkalies (Na ₂ O + K ₂ O)	62	−418.2	72.9
Sulfur trioxide (SO ₃)	80	−437.9	132.7
Phosphorus pentoxide (P ₂ O ₅) ¹	142	−1505.99	114.19

¹Woods and Garrels (1987).

Source: Eisermann *et al.* (1980)

(16.9), respectively. For example, the chemical and physical exergies for carbon dioxide gas can be expressed as:

$$Ex_{CO_2}^{ch} = b_1 \left[\epsilon_{CO_2}^o + R_u T_o \left\{ \ln \left(\frac{b_1}{\sum_i b_i} \right) \right\} \right] \quad (16.46)$$

$$Ex_{CO_2}^{ph} = b_1 [(\bar{h}_P - \bar{h}_o) - T_o(\bar{s}_P - \bar{s}_o)] \quad (16.47)$$

To find the energy and exergy flow rates with ash, the standard enthalpy and standard entropy of both biomass and coal ashes are calculated from their actual compositions (Table 16.3). The standard enthalpy of ash is computed by summing the products of the weight percent and the standard enthalpy for each of the ash constituents. Similarly, the standard entropy of ash is calculated by adding the products of the weight percent and the standard entropy of each of the ash constituents. The molecular weights, standard enthalpies, and standard entropies of selected ash constituents are given in Table 16.8. Changes in enthalpy and entropy are calculated as:

$$\Delta h_{ash} = C_{p,ash}(T - T^o) \quad (16.48)$$

$$\Delta s = c_p \ln \frac{T}{T_o} \quad (16.49)$$

As seen in Figure 16.5, water enters the super heater at state 15 and is heated to the temperature of state 7. Similarly, steam enters the reheater at state 8 and exits at state 10. The flue gases after exchanging heat with water exit through the stack to the environment. The energy and exergy balance equations for heat exchangers are:

$$\sum_i \dot{n}_{fg} \bar{h}_{fg} + \dot{m}_{fa} \Delta h_{fa} + \dot{Q}_{ub} = \sum_i \dot{n}_{st} \bar{h}_{st} + \dot{m}_s [(h_7 - h_{15}) + (1 - y)(h_{10} - h_8)] \quad (16.50)$$

$$\sum_i \dot{Ex}_{fg} + \dot{Ex}_{fa} + \dot{Ex}_{15} + \dot{Ex}_8 = \sum_e \dot{Ex}_{st} + \dot{Ex}_{10} + \dot{Ex}_8 + \dot{I}_{rs} \quad (16.51)$$

where $\dot{n}_{fg}$, $\bar{h}_{fg}$, $\dot{m}_{fa}$, Δh_{fa} , $\dot{Q}_{ub}$, $\dot{n}_{st}$, $\bar{h}_{st}$, $\dot{m}_s$, h_{15} , h_7 , h_8 , h_{10} , and y denote respectively molar flow rate of flue gases leaving the furnace, molar enthalpy of flue gases leaving the furnace, mass flow rate of fly ash, enthalpy change of fly ash, the heat loss associated with incombustibles in the fly ash exiting the stack, molar flow rate of flue gases leaving through stack, enthalpy of flue gases leaving through stack, mass flow rate of steam produced, specific enthalpy of feed water entering super heater, specific enthalpy of steam leaving super heater, specific enthalpy of steam entering

reheater, specific enthalpy of steam leaving reheater, and fraction of steam diverted towards open feed water heater.

In equation (16.51), $\dot{I}_{rs}$ denote the irreversibility rate of the heat exchangers, and $\dot{E}x_{fg}$, $\dot{E}x_{fa}$, $\dot{E}x_{st}$, $\dot{E}x_{15}$, $\dot{E}x_7$, $\dot{E}x_{10}$, and $\dot{E}x_8$ denote respectively the exergy flow rates of flue gases leaving the furnace, fly ash, flue gases leaving the stack, feed water entering the super heater, steam leaving the super heater, steam entering the reheater, and steam leaving the reheater. The chemical exergy of the flue gases leaving the stack is the same as that of the gases leaving the furnace because their chemical compositions are the same. The physical exergy of the flue gases can be calculated with equation (16.7), and depends on the stack temperature, which is assumed to be 150°C. The flows at states 7 to 15 only possess physical exergy, which can be evaluated with equation (16.7).

16.6.3.2 Analysis of high pressure turbine

The steam generated in the boiler expands from state 7 to state 8 through high pressure turbine, for which energy and exergy balances, respectively, are:

$$\dot{W}_{HPT} = \dot{m}_s(h_7 - h_8) \quad (16.52)$$

$$\dot{E}x_7 = \dot{E}x_8 + \dot{W}_{HPT} + \dot{I}_{HPT} \quad (16.53)$$

16.6.3.3 Analysis of low pressure turbine

After expansion through the high pressure turbine, a fraction y of the steam is directed at state 8 to the open feed water heater, while the remaining steam after reheating expands through the low pressure turbine. Energy and exergy balances, respectively, for low pressure turbine are:

$$\dot{W}_{LPT} = (1 - y)\dot{m}_s(h_{10} - h_{11}) \quad (16.54)$$

$$\dot{E}x_{10} = \dot{E}x_{11} + \dot{W}_{LPT} + \dot{I}_{LPT} \quad (16.55)$$

16.6.3.4 Analysis of condenser

The exhaust steam from the low pressure turbine enters the condenser at state 11 and leaves at state 12. A cooling water stream enters at 8°C and exits at 16°C. The heat released by the steam is absorbed by the cooling water stream, and energy and exergy balances, respectively, can be written as:

$$\dot{Q}_{condenser} = (1 - y)\dot{m}_s(h_{11} - h_{12}) = \dot{m}_{cw}(h_{17} - h_{16}) \quad (16.56)$$

$$\dot{E}x_{11} + \dot{E}x_{16} = \dot{E}x_{12} + \dot{E}x_{17} + \dot{I}_{condenser} \quad (16.57)$$

The mass flow rate of the cooling water is found by rearranging equation (16.56):

$$\dot{m}_{cw} = \frac{(1 - y)\dot{m}_s(h_{11} - h_{12})}{h_{17} - h_{16}} \quad (16.58)$$

16.6.3.5 Analysis of condensate pump

Water as a saturated liquid enters condensate pump where its pressure is raised to the open feed water heater pressure. The respective energy and exergy balances are:

$$\dot{W}_{CP} = (1 - y)\dot{m}_s(h_{13} - h_{12}) \quad (16.59)$$

$$\dot{E}x_{12} = \dot{E}x_{13} + \dot{W}_{CP} + \dot{I}_{CP} \quad (16.60)$$

16.6.3.6 Analysis of boiler feed pump

The pump power input can be expressed with an energy balance. Energy and exergy balances for boiler feed pump, respectively, can be expressed as:

$$\dot{W}_{BFP} = \dot{m}_s(h_{15} - h_{14}) \quad (16.61)$$

$$\dot{E}x_{14} = \dot{E}x_{15} + \dot{W}_{BFP} + \dot{I}_{BFP} \quad (16.62)$$

16.6.3.7 Analysis of open feed water heater

Mass and energy balances for the open feed water heater can be employed to find the fraction of the extracted fraction y . Respective energy and exergy balances for this device can be expressed as:

$$y = \frac{h_{14} - h_{13}}{h_9 - h_{13}} \quad (16.63)$$

$$\dot{E}x_9 + \dot{E}x_{13} = \dot{E}x_{14} + \dot{I}_{FWH} \quad (16.64)$$

16.6.4 Boiler and overall energy and exergy efficiencies

The energy efficiency of boiler and plant can be expressed as:

$$\eta_{boiler} = \frac{\dot{m}_s[(h_7 - h_{15}) + (1 - y)(h_8 - h_{10})]}{\dot{m}_c HHV_c + \dot{m}_b HHV_b} \quad (16.65)$$

$$\eta_{plant} = \frac{\dot{W}_{HPT} + \dot{W}_{LPT} - \dot{W}_{pump,1} - \dot{W}_{pump,2}}{\dot{m}_c HHV_c + \dot{m}_b HHV_b} \quad (16.66)$$

Similarly, the exergy efficiencies for boiler and plant can be written as:

$$\Psi_{boiler} = \frac{\dot{E}x_7 + \dot{E}x_{10} - \dot{E}x_{15} - \dot{E}x_8}{\dot{m}_c ex_c^{ch} + \dot{m}_b ex_b^{ch}} \quad (16.67)$$

$$\Psi_{plant} = \frac{\dot{W}_{HPT} + \dot{W}_{LPT} - \dot{W}_{pump,1} - \dot{W}_{pump,2}}{\dot{m}_c ex_c^{ch} + \dot{m}_b ex_b^{ch}} \quad (16.68)$$

16.7 EFFECT OF BIOMASS CO-FIRING ON COAL POWER GENERATION SYSTEMS

The effect of biomass co-firing on coal power generation systems is examined for various fuel blends. We consider two types of coal and four types of biomass that span the range of typical fuels in each category. We investigate energy and exergy inputs and the useful outputs for the overall plant and energy and exergy losses for its components, as well as the effect of co-firing on energy and exergy efficiencies and gaseous emissions of CO_2 , NO_x , and SO_x for the boiler and the plant. Values reported here are determined with Engineering Equation Solver.

Acronyms are used as described here to denote the combinations of fuels considered. The acronym for a fuel mixture blend is based on the first letter of the coal and first and last letters of the biomass. For example, the acronym for the bituminous and rice husk blend would be B/RH.

Two cases are considered: fixed fuel flow (case 1) and fixed heat input to the steam cycle (case 2). Graphs presented in this section are adapted from Mehmood (2011). All graphs for case 1 are plotted against co-firing ratio. Since, the second case involves different co-firing ratios due to a varying fuel mass flow rate; graphs for this case are plotted against coal flow rate. This is done because the coal flow rate is constant at a particular co-firing condition for all fuel blends and the two cases considered.

The co-firing share of coal P_c and the co-firing share of biomass P_b , also called the co-firing ratio, are defined as:

$$P_c = \frac{\text{mass of coal}}{(\text{mass of coal}) + (\text{mass of biomass})} \times 100 \quad (16.69)$$

$$P_b = \frac{\text{mass of biomass}}{(\text{mass of coal}) + (\text{mass of biomass})} \times 100 \quad (16.70)$$

Table 16.9. Overall system performance parameters for bituminous coal/biomass blends based on a fixed fuel flow rate¹.

Fuel blend	Fuel flow rate		Co-firing share		Input			Output		
	$\dot{m}_c$ [kg/s]	$\dot{m}_b$ [kg/s]	P_c [%]	P_b [%]	Air [mol/s]	$\dot{E}$ [MW]	$\dot{E}_x$ [MW]	$\dot{Q}$ [MW]	$\dot{W}_{net}$ [MW]	$\dot{E}_{x_u}$ [MW]
Base ²	1	0	100	0	79.86	28.33	29.30	24.65	9.92	13.74
B/RH	0.95	0.05	95	5	77.85	27.66	28.66	24.04	9.67	13.43
	0.90	0.10	90	10	75.83	27.00	28.02	23.42	9.43	13.09
	0.85	0.15	85	15	73.81	26.33	27.38	22.80	9.18	12.74
	0.80	0.20	80	20	71.79	25.66	26.74	22.18	8.93	12.40
	0.75	0.25	75	25	69.77	24.99	26.10	21.56	8.68	12.06
B/SD	0.70	0.30	70	30	67.76	24.33	25.51	20.95	8.43	11.70
	0.95	0.05	95	5	78.10	27.78	28.79	24.14	9.71	13.49
	0.90	0.10	90	10	76.34	27.23	28.29	23.62	9.51	13.20
	0.85	0.15	85	15	74.58	26.67	27.78	23.10	9.30	12.91
	0.80	0.20	80	20	72.81	26.12	27.27	22.58	9.09	12.61
B/CL	0.75	0.25	75	25	71.05	25.57	26.77	22.06	8.88	12.32
	0.70	0.30	70	30	69.29	25.02	26.34	21.54	8.67	12.03
	0.95	0.05	95	5	77.91	27.63	28.58	24.00	9.66	13.41
	0.90	0.10	90	10	75.99	26.92	27.86	23.35	9.40	13.05
	0.85	0.15	85	15	74.03	26.22	27.14	22.69	9.14	12.69
B/RFD	0.80	0.20	80	20	72.10	25.51	26.42	22.04	8.87	12.32
	0.75	0.25	75	25	70.13	24.81	25.70	21.39	8.61	11.96
	0.70	0.30	70	30	68.19	24.10	24.73	20.74	8.34	11.45
	0.95	0.05	95	5	77.92	27.75	28.74	24.11	9.70	13.48
	0.90	0.10	90	10	75.98	27.16	28.19	23.56	9.49	13.17
	0.85	0.15	85	15	74.02	26.57	27.64	23.02	9.27	12.87
	0.80	0.20	80	20	72.09	25.99	27.08	22.48	9.05	12.56
	0.75	0.25	75	25	70.14	25.40	26.53	21.93	8.83	12.25
	0.70	0.30	70	30	68.20	24.82	25.87	21.39	8.61	11.87

¹ $\dot{m}_c$, $\dot{m}_b$, P_c , P_b , $\dot{E}$, $\dot{E}_x$, $\dot{Q}$, $\dot{W}_{net}$, and $\dot{E}_{x_u}$ denote mass flow rate of coal, mass flow rate of biomass, percent co-firing share of coal, percent co-firing share of biomass (or co-firing ratio), energy input rate, exergy input rate, useful heat input to the steam cycle, useful exergy input to the steam cycle, and net power output of the plant.

²B/RH, B/SD, B/CL, and B/RFD respectively denote fuel blends bituminous coal/rice husk, bituminous coal/sawdust, bituminous coal/chicken litter, and bituminous coal/refuse derived fuel.

16.7.1 Effect of co-firing on overall system performance

The inputs and outputs for the overall plant are listed in Table 16.9 for bituminous coal/biomass blends based on a fixed overall fuel flow rate. These data show that energy input, exergy input, and air flow rates to the plant decrease with the addition of biomass. The corresponding heat produced in the boiler, and the useful exergy and network outputs decrease with the addition of biomass.

The decrease in energy and exergy inputs depends on the heating value of biomass, which is a measure of its energy density. Chicken litter has the lowest heating value of the biomass fuels considered here, so the largest reductions in energy input and exergy input are observed for bituminous coal/chicken litter blends. In contrast, sawdust has the highest heating of the considered biomass fuels, so the decreases in energy and exergy inputs are the smallest for bituminous coal/sawdust blends. Relative to a baseline of 100% coal firing, the energy input decreases by 14.1, 11.7, 14.9, and 12.4%, respectively, for fuel blends of bituminous coal/rice husk, bituminous coal/sawdust, bituminous coal/chicken litter, and bituminous coal/refuse derived

fuel, when the co-firing share of biomass (co-firing ratio) increases to 30%. Correspondingly, exergy input reductions of 12.93, 10.10, 15.60, and 11.71% respectively are observed at a 30% co-firing ratio for blends of bituminous coal/rice husk, bituminous coal/sawdust, bituminous coal/chicken litter, and bituminous coal/refuse derived fuel.

With less energy input, less air is needed. The decrease in air flow rate also depends on the oxygen and nitrogen contents of the biomass fuel. All considered biomass fuels have more oxygen content than bituminous coal, so the amount of oxygen required for combustion decreases with the addition of biomass to a blend. Moreover, all considered biomass types, except chicken litter, contain less nitrogen than bituminous coal, so the addition of biomass (except chicken litter) to a blend further decreases the oxygen required for oxidation of fuel nitrogen to nitric oxide and nitrogen dioxide. Relative to the baseline, the air flow rate decreases at a 30% co-firing ratio by 15.2, 13.2, 14.6, and 14.6% respectively for fuel blends of bituminous coal/rice husk, bituminous coal/sawdust, bituminous coal/chicken litter, and bituminous coal/refuse derived fuel.

It can also be observed in Table 16.9 that about 87% of total energy supplied to the boiler is transferred to the steam cycle as useful heat, while around 40% of this useful heat is converted to power. In contrast, 47% of total exergy input to the boiler is supplied by water. Decreases in input parameters reduce the output parameters. The reductions in output parameters are the greatest for the bituminous coal/chicken litter blend and the smallest for the bituminous coal/sawdust blend. As the co-firing ratio increases from 0 to 30%, the output parameters decrease by approximately 15, 12.5, 16, and 13% respectively for fuel blends of bituminous coal/rice husk, bituminous coal/sawdust, bituminous coal/chicken litter, and bituminous coal/refuse derived fuel.

Overall system performance parameters for lignite/biomass blends based on a fixed fuel flow are listed in Table 16.10. The higher heating value of the lignite selected considered here is 20.07 kJ/kg. Lignite is a low-grade coal, so relative to bituminous coal it provides less energy and exergy per unit mass, produces less heat via combustion and requires less air for combustion. The compositions and heating values of the selected biomass fuels between are more similar to lignite than to bituminous coal, so relatively smaller reductions in performance parameters are observed in Table 16.10 for lignite/biomass blends than bituminous coal/biomass blends.

The reductions in energy input and exergy inputs are observed to be the greatest for lignite/chicken litter blends and the smallest for lignite/sawdust blends. With respect to the baseline (0% co-firing ratio), the energy input decreases at a 30% co-firing ratio by 7.6, 4.2, 8.7 and 5.1% respectively for fuel blends of lignite/rice husk, lignite/sawdust, lignite/chicken litter, and lignite/refuse derived fuel. The corresponding reductions in exergy input are 6.6, 2.8, 8.8, and 4.1%.

As with bituminous coal/ biomass blends, the highest and the lowest decreases in air flow rate occur for blends of lignite/rice husk and lignite/sawdust, respectively. Relative to the baseline, air flow rate reductions of 8.3, 5.5, 7.5, and 7.5% respectively are observed at 30% co-firing ratio for blends of lignite/rice husk, lignite/sawdust, lignite/chicken litter, and lignite/refuse derived fuel.

Approximately 85% of total energy supplied by lignite to the boiler is seen in Table 16.10 to be transferred to steam cycle as useful heat, while around 40% of this useful heat is converted to power.

In addition, around 45% of the total exergy input to the boiler is supplied by water. With respect to baseline, the output parameter decreases range from 4.5 to 9.5% for all lignite/biomass blends at a 30% co-firing ratio. The greatest and smallest reductions found in output parameters are observed for blends of lignite/chicken litter and lignite/sawdust, respectively. Relative to the baseline, decreases in output parameters of about 9.5% and 5.0% respectively are observed at 30% co-firing ratio for blends of lignite/chicken litter and lignite/sawdust.

Overall system performance parameters are listed in Tables 16.11 and 16.12 for coal/biomass blends based on fixed heat input to steam cycle (case 2). Coal and biomass flow rates for this case are shown in Figure 16.6 for all fuel blends. For case 2, the steam cycle conditions not vary, so output parameters for blends of bituminous coal/biomass and lignite/biomass are same at all co-firing ratios, as shown in Tables 16.11 and 16.12. In addition, the energy and exergy inputs increase with the addition of biomass to the fuel blend. The losses associated with biomass moisture and ash necessitates the provision of more biomass than coal to maintain a constant heat

Table 16.10. Overall system performance parameters for lignite/biomass blends based on a fixed fuel flow rate¹.

Fuel blend	Fuel flow rate		Co-firing share		Input			Output		
	$\dot{m}_c$ [kg/s]	$\dot{m}_b$ [kg/s]	P_c [%]	P_b [%]	Air [mol/s]	$\dot{E}$ [MW]	$\dot{E}_x$ [MW]	$\dot{Q}$ [MW]	$\dot{W}_{net}$ [MW]	$\dot{E}_{x_u}$ [MW]
Base ¹	1	0	100	0	54.53	20.07	21.22	17.00	6.84	9.48
L/RH	0.95	0.05	95	5	53.75	19.82	20.99	16.76	6.75	9.36
	0.90	0.10	90	10	53.00	19.56	20.75	16.53	6.65	9.23
	0.85	0.15	85	15	52.25	19.31	20.52	16.29	6.56	9.09
	0.80	0.20	80	20	51.50	19.05	20.28	16.06	6.46	8.96
	0.75	0.25	75	25	50.75	18.80	20.05	15.82	6.37	8.83
L/SD	0.70	0.30	70	30	50.00	18.54	19.82	15.59	6.27	8.70
	0.95	0.05	95	5	54.01	19.93	21.12	16.85	6.79	9.41
	0.90	0.10	90	10	53.51	19.79	21.02	16.73	6.73	9.33
	0.85	0.15	85	15	53.02	19.65	20.92	16.58	6.67	9.25
	0.80	0.20	80	20	52.52	19.51	20.81	16.44	6.62	9.18
L/CL	0.75	0.25	75	25	52.03	19.37	20.71	16.29	6.56	9.10
	0.70	0.30	70	30	51.53	19.23	20.63	16.18	6.51	9.02
	0.95	0.05	95	5	53.82	19.78	20.91	16.73	6.73	9.34
	0.90	0.10	90	10	53.14	19.49	20.60	16.47	6.63	9.19
	0.85	0.15	85	15	52.47	19.20	20.29	16.20	6.52	9.04
L/RFD	0.80	0.20	80	20	51.79	18.90	19.98	15.94	6.41	8.89
	0.75	0.25	75	25	51.12	18.61	19.67	15.65	6.31	8.74
	0.70	0.30	70	30	50.44	18.32	19.34	15.39	6.19	8.59
	0.95	0.05	95	5	53.83	19.90	21.08	16.85	6.78	9.40
	0.90	0.10	90	10	53.15	19.73	20.93	16.67	6.71	9.31
	0.85	0.15	85	15	52.48	19.55	20.78	16.53	6.65	9.22
	0.80	0.20	80	20	51.80	19.38	20.63	16.35	6.58	9.13
	0.75	0.25	75	25	51.13	19.21	20.49	16.20	6.52	9.04
	0.70	0.30	70	30	50.45	19.04	20.35	16.03	6.45	8.95

¹L/RH: lignite/rice husk blend, L/SD: lignite/sawdust blend, L/CL: lignite/chicken litter blend, L/RFD: lignite/refuse derived fuel blend.

rate in the boiler. Hence, the energy and exergy inputs increase as the biomass fraction in the blend rises.

The amount of additional biomass required to produce the same heat as can be produced by burning 1 kg/s of coal is observed in Tables 16.11 and 16.12 to depend on the energy content of the biomass. The largest amounts of biomass are required for chicken litter blends and the lowest for sawdust blends.

The additional biomass required producing same heat as burning 1 kg/s of coal is seen in Table 16.12 to be smaller for lignite/biomass co-firing than bituminous coal/biomass co-firing. When the coal flow rate decreases from 1.0 to 0.7 kg/s, the mass flow rates of chicken litter are 0.64 kg/s and 0.44 kg/s for blends of bituminous coal/chicken litter and lignite/chicken litter respectively, which are about 113% and 47% more than for case 1.

A slight decrease in air flow rate relative to no co-firing is observed with the addition of biomass to the mixture for all fuel blends, except bituminous coal/chicken litter and lignite/chicken litter. For bituminous coal/biomass blends, the oxygen required for combustion decreases with the addition of biomass since the biomass fuels contain more oxygen than bituminous coal. Since all considered biomass types except chicken litter contain less nitrogen than bituminous coal, the addition of biomass fuels except chicken litter to fuel blends further decreases the oxygen

Table 16.11. Overall system performance parameters for bituminous coal/biomass blends based on fixed heat input to steam cycle.

Fuel blend	Fuel flow rate		Co-firing share		Input			Output		
	$\dot{m}_c$ [kg/s]	$\dot{m}_b$ [kg/s]	P_c [%]	P_b [%]	Air [mol/s]	$\dot{E}$ [MW]	$\dot{E}_x$ [MW]	$\dot{Q}$ [MW]	$\dot{W}_{net}$ [MW]	$\dot{E}_{x_u}$ [MW]
Base	1	0	100	0	79.86	28.33	29.30	24.65	9.92	13.74
B/RH	0.95	0.10	90.45	9.55	79.80	28.40	29.47	24.65	9.92	13.74
	0.90	0.20	81.77	18.23	79.80	28.49	29.66	24.65	9.92	13.74
	0.85	0.30	73.85	26.15	79.70	28.58	29.85	24.65	9.92	13.74
	0.80	0.40	66.59	33.41	79.70	28.66	30.04	24.65	9.92	13.74
	0.75	0.50	59.91	40.09	79.70	28.75	30.23	24.65	9.92	13.74
B/SD	0.70	0.60	53.76	46.24	79.70	28.84	30.43	24.65	9.92	13.74
	0.95	0.09	91.63	8.37	79.70	28.40	29.48	24.65	9.92	13.74
	0.90	0.17	83.84	16.16	79.60	28.48	29.68	24.65	9.92	13.74
	0.85	0.26	76.56	23.44	79.50	28.57	29.88	24.65	9.92	13.74
	0.80	0.35	69.74	30.26	79.30	28.65	30.08	24.65	9.92	13.74
B/CL	0.75	0.43	63.36	36.64	79.20	28.73	30.28	24.65	9.92	13.74
	0.70	0.52	57.35	42.65	79.10	28.81	30.45	24.65	9.92	13.74
	0.95	0.11	89.97	10.03	80.20	28.41	29.40	24.65	9.92	13.74
	0.90	0.21	80.95	19.05	80.50	28.50	29.51	24.65	9.92	13.74
	0.85	0.32	72.79	27.21	80.90	28.59	29.63	24.65	9.92	13.74
B/RFD	0.80	0.42	65.37	34.63	81.20	28.68	29.74	24.65	9.92	13.74
	0.75	0.53	58.60	41.40	81.60	28.78	29.85	24.65	9.92	13.74
	0.70	0.64	52.40	47.60	82.00	28.87	29.98	24.65	9.92	13.74
	0.95	0.09	91.38	8.62	79.50	28.39	29.45	24.65	9.92	13.74
	0.90	0.18	83.40	16.60	79.20	28.46	29.62	24.65	9.92	13.74
	0.85	0.27	75.97	24.03	78.90	28.54	29.79	24.65	9.92	13.74
	0.80	0.36	69.05	30.95	78.60	28.61	29.96	24.65	9.92	13.74
	0.75	0.45	62.59	37.41	78.20	28.68	30.12	24.65	9.92	13.74
	0.70	0.54	56.55	43.45	77.90	28.76	30.30	24.65	9.92	13.74

required for oxidation of fuel nitrogen to nitric oxide and nitrogen dioxide. The respective oxygen and nitrogen contents of chicken litter are 1.45 and 3.27 times that of bituminous coal, necessitating additional oxygen for oxidation of the nitrogen. Hence, the air flow rate increases as the chicken litter fraction increases in the blend. Chicken litter contains less oxygen and more nitrogen than lignite, so relative to the baseline more oxygen is required to combustion lignite/biomass blends, resulting in increased air flow rates.

16.7.2 Effect of co-firing on energy and exergy losses

Energy losses are made up of waste energy emissions to the environment. However, exergy losses are comprised of two types: waste exergy emissions to the environment (or external exergy losses) and internal exergy destructions (or internal exergy losses) caused by irreversibilities. Energy losses and external exergy losses associated with the boiler are due to moisture in fuel, exit flue gases, ash, unburned combustibles, and radiation and convection from the furnace exterior. Energy losses and exergy losses associated with steam cycle components are due to heat rejection from the condenser and irreversibilities. In this section, energy losses and external exergy losses are discussed together. The effect of co-firing on irreversibilities is investigated separately. The furnace exit gas temperature is an important performance measure for the boiler as heat transfer between the furnace exit gas and feed water depends upon it. The impact of co-firing on the furnace exit gas temperature is also explored in this section.

Table 16.12. Overall system performance parameters for lignite/biomass blends based on fixed heat input to steam cycle.

Fuel blend	Fuel flow rate		Co-firing share		Input			Output		
	$\dot{m}_c$ [kg/s]	$\dot{m}_b$ [kg/s]	P_c [%]	P_b [%]	Air [mol/s]	$\dot{E}$ [MW]	$\dot{E}_x$ [MW]	$\dot{Q}$ [MW]	$\dot{W}_{net}$ [MW]	$\dot{E}_{x_u}$ [MW]
Base	1	0	100	0	54.53	20.07	21.22	17.00	6.84	9.48
L/RH	0.95	0.07	93.27	6.73	54.51	20.10	21.30	17.00	6.84	9.48
	0.90	0.14	86.74	13.26	54.49	20.13	21.38	17.00	6.84	9.48
	0.85	0.21	80.44	19.56	54.48	20.16	21.46	17.00	6.84	9.48
	0.80	0.28	74.36	25.64	54.47	20.19	21.54	17.00	6.84	9.48
	0.75	0.34	68.50	31.50	54.46	20.22	21.63	17.00	6.84	9.48
L/SD	0.70	0.41	62.84	37.16	54.45	20.26	21.69	17.00	6.84	9.48
	0.95	0.06	94.12	5.88	54.42	20.09	21.31	17.00	6.84	9.48
	0.90	0.12	88.31	11.69	54.36	20.12	21.39	17.00	6.84	9.48
	0.85	0.18	82.62	17.38	54.30	20.15	21.48	17.00	6.84	9.48
	0.80	0.24	77.03	22.97	54.25	20.18	21.57	17.00	6.84	9.48
L/CL	0.75	0.30	71.54	28.46	54.19	20.21	21.65	17.00	6.84	9.48
	0.70	0.36	66.16	33.84	54.13	20.24	21.74	17.00	6.84	9.48
	0.95	0.07	92.92	7.08	54.74	20.10	21.26	17.00	6.84	9.48
	0.90	0.15	86.10	13.90	55.01	20.13	21.29	17.00	6.84	9.48
	0.85	0.22	79.57	20.43	55.28	20.17	21.31	17.00	6.84	9.48
L/RFD	0.80	0.29	73.31	26.69	55.54	20.21	21.34	17.00	6.84	9.48
	0.75	0.36	67.32	32.68	55.81	20.24	21.36	17.00	6.84	9.48
	0.70	0.44	61.56	38.44	56.08	20.28	21.39	17.00	6.84	9.48
	0.95	0.06	93.95	6.05	54.29	20.09	21.29	17.00	6.84	9.48
	0.90	0.12	87.99	12.01	54.09	20.11	21.36	17.00	6.84	9.48
	0.85	0.18	82.16	17.84	53.89	20.13	21.42	17.00	6.84	9.48
	0.80	0.25	76.46	23.54	53.70	20.15	21.49	17.00	6.84	9.48
	0.75	0.31	70.89	29.11	53.50	20.18	21.56	17.00	6.84	9.48
	0.70	0.37	65.44	34.56	53.30	20.20	21.60	17.00	6.84	9.48

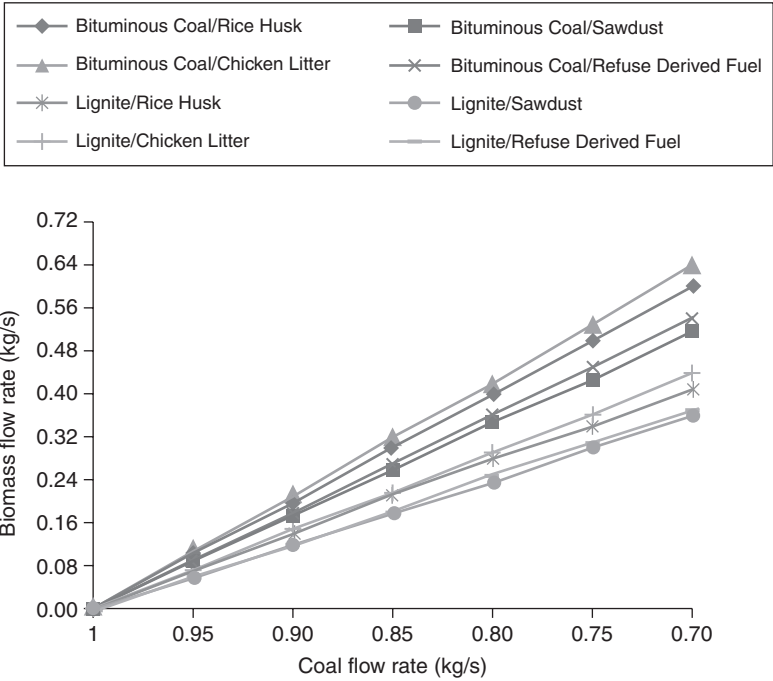


Figure 16.6. Comparison of coal and biomass flow rates based on fixed heat input to steam cycle.

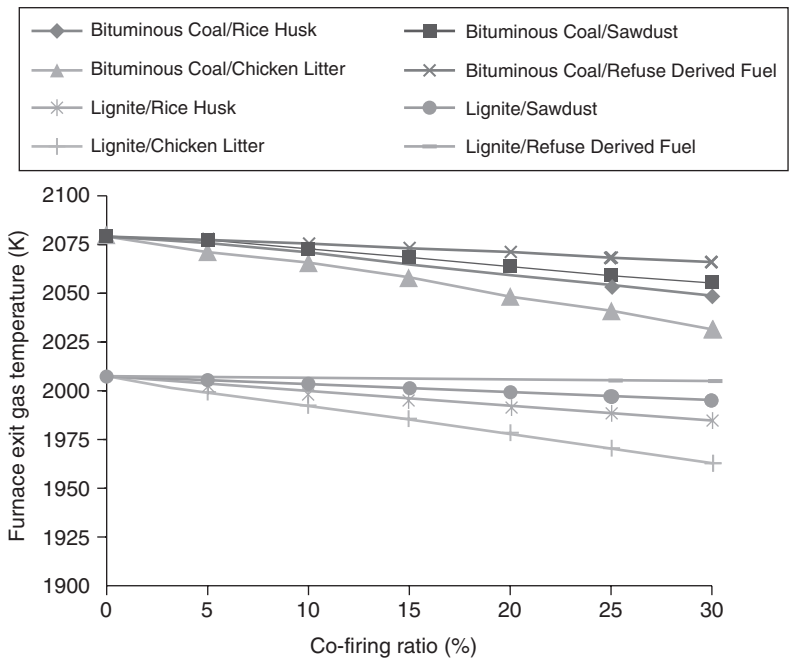


Figure 16.7. Effect of co-firing on furnace exit gas temperature based on a fixed fuel flow rate.

16.7.2.1 Effect of co-firing on furnace exit gas temperature

The furnace exit gas temperature decreases with increasing biomass content for all blends, as shown in Figure 16.7. The extent of decrease in the furnace exit gas temperature depends on the heating value, moisture content, and ash content of biomass fuels. Biomass with a low heating value provides little energy input. High biomass moisture content requires part of the heat supplied to be used to vaporize the moisture. High ash content results in more sensible heat leaving the combustion chamber with solid waste. These factors lower the furnace exit gas temperature. Among the considered biomass types, chicken litter has the lowest calorific value and the highest ash content. It also contains more moisture than bituminous coal. Therefore, the largest reductions in furnace exit gas temperature are observed for the bituminous coal/chicken litter and lignite/chicken litter blends. When the co-firing ratio increases from 0 to 30%, for instance, the furnace exit gas temperature decreases from 2079 to 2031 K for the bituminous coal/chicken litter blend and from 2007 to 1962 K for the lignite/chicken litter blend.

It is also found that the moisture content of biomass has a much more significant effect than the ash content on the reduction of furnace exit gas temperature. Refuse derived fuel has much higher ash content than sawdust, which has a much higher moisture content than refuse derived fuel. The higher moisture content of sawdust requires more heat to be supplied for the latent heat of vaporization during its combustion compared to refuse derived fuel. Hence, a more pronounced decrease in furnace exit gas temperature is observed for the bituminous coal/sawdust blend than for the bituminous coal/refuse derived fuel blend. Similarly, lignite has higher calorific value and lower ash content than that of refuse derived fuel, but contains about 8% more moisture. Much more heat is needed to vaporize the moisture of lignite than of refuse derived fuel, diminishing the difference between heating values of these two fuels. Thus, the furnace exit gas temperature decreases the least for the lignite/refuse derived fuel blend compared to all other blends. With respect to base coal, the furnace exit gas temperature decreases to 2066 and 2004 K, respectively, for blends of bituminous coal/refuse derived fuel and lignite/refuse derived fuel, at a 30% co-firing ratio.

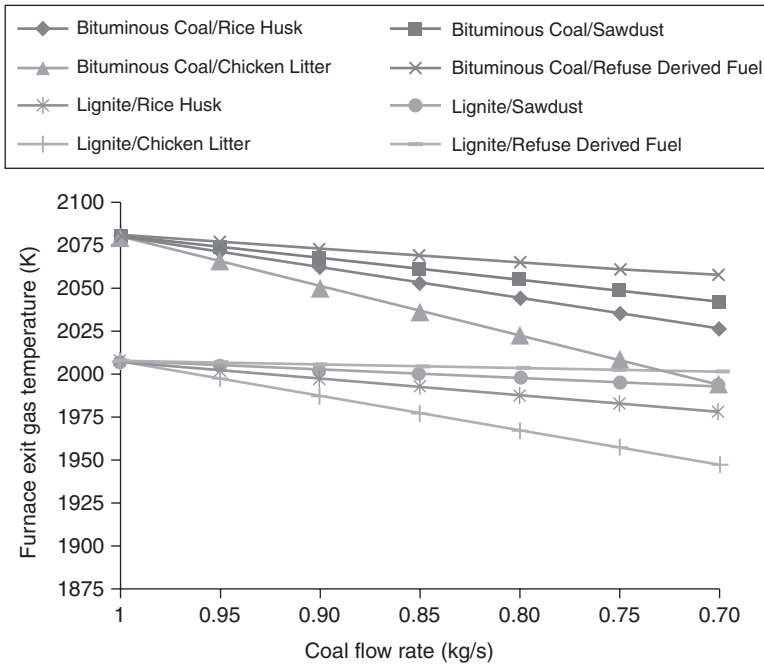


Figure 16.8. Effect of co-firing on furnace exit gas temperature based on a fixed heat input to the steam cycle.

The decreases in furnace exit gas temperature are observed to be more pronounced for case 2 than case 1 due to a larger amount of biomass being fed to the boiler, as shown in Figure 16.8. The trends for case 2 are same as for case 1. The furnace exit gas temperature decreases from 2079 to 1994 K for the bituminous coal/chicken litter blend and from 2007 to 2001 K for the lignite/chicken litter blend, when the coal flow rate decreases from 1 kg/s to 0.7 kg/s. Similar to case 1, the furnace exit gas temperature decreases the least for the lignite/refuse derived fuel blend compared to all other blends. For an input rate of 0.7 kg/s of coal, the furnace exit gas temperature decreases to 2057 and 2001 K for the blends of bituminous coal/refuse derived fuel and lignite/refuse derived fuel, respectively.

16.7.2.2 Effect of co-firing on energy losses and external exergy losses

Table 16.13 illustrates energy losses and external exergy losses of the system for bituminous coal/biomass blends based on a fixed fuel flow. For 100% coal, the overall plant energy losses and external exergy losses are about 65% of the energy input and 14% of the exergy input respectively. About 53% of the energy losses occur in the condenser. Moreover, energy losses associated with the boiler are about 13% of the energy input. Energy and exergy losses due to ash as well as radiation and convection from the furnace exterior surface are negligible. Energy and exergy losses associated with flue gas are seen to be 6% of the energy input and 10% of the exergy input respectively, whereas, energy and exergy losses due to moisture are about 4% of the energy input and 4.50% of the exergy input respectively. Heat losses due to unburned combustibles and radiation and convection are 3% of the energy input, as assumed.

Energy and exergy losses due to fuel moisture increase with the addition of biomass to a blend for all blends except bituminous coal/refuse derived fuel, as seen in Table 16.13. This result is because all considered biomass types, except refuse derived fuel, contain more moisture than bituminous coal. For this reason, energy and exergy losses due to moisture increase for the blends of bituminous coal/rice husk, bituminous coal/sawdust and bituminous coal/chicken

Table 16.13. Effect of co-firing on energy losses and external exergy losses for bituminous coal/biomass blends based on a fixed fuel flow rate¹.

Fuel blend	Co-firing share [%]		Energy loss rate [MW]					Exergy loss rate [MW]			
	P_c	P_b	M	FG	Ash	$\dot{Q}$	$\dot{Q}_{cond}$	M	FG	Ash	$\dot{E}x_h$
Base	100	0	1.237	1.630	0.021	0.850	14.52	1.319	2.469	0.013	0.070
B/RH	95	5	1.257	1.590	0.022	0.830	14.16	1.341	2.409	0.013	0.068
	90	10	1.277	1.549	0.022	0.810	13.80	1.362	2.349	0.013	0.066
	85	15	1.297	1.509	0.023	0.790	13.44	1.383	2.290	0.014	0.065
	80	20	1.316	1.468	0.023	0.770	13.08	1.404	2.230	0.014	0.063
	75	25	1.336	1.428	0.024	0.750	12.71	1.425	2.171	0.014	0.061
B/SD	70	30	1.356	1.388	0.024	0.730	12.34	1.446	2.111	0.014	0.059
	95	5	1.297	1.595	0.020	0.833	14.23	1.383	2.417	0.012	0.069
	90	10	1.356	1.560	0.019	0.817	13.92	1.446	2.365	0.012	0.067
	85	15	1.416	1.525	0.018	0.800	13.61	1.510	2.312	0.011	0.066
	80	20	1.475	1.490	0.017	0.784	13.30	1.573	2.260	0.011	0.064
B/CL	75	25	1.534	1.454	0.016	0.767	12.99	1.637	2.208	0.010	0.063
	70	30	1.594	1.419	0.015	0.750	12.68	1.700	2.156	0.010	0.061
	95	5	1.249	1.590	0.024	0.829	14.14	1.332	2.409	0.015	0.068
	90	10	1.261	1.551	0.026	0.808	13.76	1.345	2.349	0.017	0.066
	85	15	1.273	1.511	0.028	0.787	13.39	1.358	2.289	0.019	0.064
B/RDF	80	20	1.285	1.471	0.030	0.765	12.99	1.370	2.230	0.021	0.062
	75	25	1.297	1.431	0.033	0.744	12.61	1.383	2.170	0.023	0.060
	70	30	1.308	1.392	0.035	0.723	12.23	1.396	2.110	0.025	0.058
	95	5	1.209	1.591	0.023	0.832	14.21	1.289	2.411	0.014	0.068
	90	10	1.180	1.552	0.024	0.815	13.88	1.259	2.353	0.015	0.067
	85	15	1.151	1.513	0.026	0.797	13.56	1.228	2.295	0.016	0.066
	80	20	1.123	1.473	0.028	0.780	13.25	1.198	2.237	0.017	0.064
	75	25	1.094	1.434	0.029	0.762	12.92	1.167	2.178	0.017	0.063
	70	30	1.066	1.395	0.031	0.745	12.61	1.137	2.120	0.018	0.061

¹ M , FG , $\dot{Q}$, $\dot{Q}_{cond}$, and $\dot{E}x_h$ denote moisture, flue gases, heat loss due to unburned combustibles and radiation and convection from the exterior surface of boiler, energy loss in condenser, and exergy loss due to radiation and convection heat transfer from the exterior surface of boiler, respectively.

litter with increasing of biomass content, and decrease for the bituminous coal/refuse derive fuel blend. Energy and exergy losses with ash also increase with increasing biomass content for the blends of bituminous coal/rice husk, bituminous coal/chicken litter blend, and bituminous coal/refuse derived fuel, because of the higher ash contents of these three biomass fuels than that of bituminous coal. However, the energy loss with the sensible heat of ash decreases for the bituminous coal/sawdust blend due to the lower ash content of sawdust than of bituminous coal.

It can be seen from Table 16.13 that energy and exergy losses due to stack gas decrease with increasing biomass in a blend. This result is due to the corresponding decrease in both furnace exit gas temperature and overall mass flow rate of flue gases. Due to the low temperature of the product gas, less heat is transferred to the environment. Increasing the biomass fraction in a blend also decreases the overall flue gas mass flow rate, which results in a further decrease in heat loss to the environment. With respect to base coal, the energy loss through stack gas decreases by 14.85, 12.94, 14.60, and 14.42% for blends of bituminous coal/rice husk, bituminous coal/sawdust, bituminous coal/chicken litter and bituminous coal/refuse derived fuel respectively, at a 30% co-firing ratio. Likewise, the exergy loss due to exhaust gas decreases by 14.50, 12.68, 14.54, and 14.14% for blends of bituminous coal/rice husk, bituminous coal/sawdust, bituminous coal/chicken litter, and bituminous coal/refuse derived fuel respectively, at a 30% co-firing ratio.

Table 16.14. Effect of co-firing on energy losses and external exergy losses for lignite/biomass blends based on a fixed fuel flow rate.

Fuel blend	Co-firing share [%]		Energy loss rate [MW]					Exergy loss rate [MW]			
	P_c	P_b	M	FG	Ash	$\dot{Q}$	$\dot{Q}_{cond}$	M	FG	Ash	$\dot{E}x_h$
Base	100	0	1.967	1.126	0.017	0.602	10.01	2.098	1.742	0.010	0.048
L/RH	95	5	1.950	1.111	0.018	0.595	9.88	2.080	1.719	0.011	0.047
	90	10	1.933	1.095	0.018	0.587	9.74	2.062	1.695	0.011	0.046
	85	15	1.917	1.080	0.019	0.579	9.60	2.044	1.672	0.012	0.046
	80	20	1.900	1.065	0.020	0.572	9.46	2.027	1.649	0.012	0.045
	75	25	1.883	1.050	0.021	0.564	9.33	2.009	1.625	0.012	0.044
L/SD	70	30	1.867	1.035	0.021	0.556	9.19	1.991	1.602	0.013	0.043
	95	5	1.990	1.116	0.016	0.598	9.93	2.122	1.726	0.010	0.047
	90	10	2.013	1.106	0.015	0.594	9.86	2.147	1.710	0.010	0.047
	85	15	2.036	1.096	0.014	0.590	9.77	2.171	1.695	0.009	0.047
	80	20	2.059	1.086	0.014	0.585	9.69	2.196	1.679	0.009	0.046
L/CL	75	25	2.082	1.076	0.013	0.581	9.60	2.220	1.664	0.008	0.046
	70	30	2.105	1.066	0.012	0.577	9.53	2.245	1.648	0.008	0.046
	95	5	1.942	1.111	0.020	0.593	9.86	2.071	1.718	0.012	0.047
	90	10	1.918	1.097	0.022	0.585	9.70	2.045	1.695	0.014	0.046
	85	15	1.893	1.082	0.025	0.576	9.55	2.019	1.671	0.016	0.045
L/RDF	80	20	1.868	1.068	0.027	0.567	9.39	1.993	1.648	0.018	0.044
	75	25	1.844	1.053	0.030	0.558	9.22	1.967	1.625	0.020	0.044
	70	30	1.819	1.039	0.032	0.550	9.07	1.940	1.601	0.023	0.043
	95	5	1.902	1.112	0.019	0.597	9.93	2.028	1.720	0.011	0.047
	90	10	1.837	1.098	0.021	0.592	9.82	1.959	1.698	0.012	0.047
	85	15	1.772	1.084	0.022	0.587	9.74	1.890	1.677	0.014	0.047
	80	20	1.707	1.070	0.024	0.581	9.64	1.820	1.655	0.015	0.046
	75	25	1.642	1.056	0.026	0.576	9.55	1.751	1.633	0.016	0.046
	70	30	1.577	1.042	0.028	0.571	9.45	1.682	1.612	0.017	0.045

Energy and external exergy losses of the system for lignite/biomass blends based on a fixed fuel flow are shown in Table 16.14. It is noted that overall plant energy losses and external exergy losses are about 68% of the energy input and 18% of the exergy input respectively when 100% lignite is used. It is also observed that around 50% energy losses occur in the condenser. Energy losses and external exergy losses for the boiler are about 18% of the energy input. Since, lignite contains more moisture than bituminous coal, it can also be observed from Table 16.14 that energy and exergy losses due to moisture for lignite are greater than those of bituminous coal. Moreover, energy and exergy losses due to flue gases and ash are smaller for lignite than for bituminous coal. Energy and exergy losses through flue gas are found to be around 5.5% of the energy input and 8% of the exergy input respectively, whereas energy and exergy losses due to moisture are about 10% of the energy input and 8% of the exergy input, respectively. Heat losses due to unburned combustibles and radiation and convection are 3% of the energy input, as assumed.

It is evident from Table 16.14 that energy and exergy losses due to moisture decrease with increasing biomass content for all blends except lignite/sawdust. Since the selected lignite has more moisture than all considered biomass types except sawdust, energy and exergy losses due to moisture decrease for blends of lignite/rice husk, lignite/refuse derived fuel and lignite/ chicken litter, with an increase of biomass in the blend. The largest decreases are found for the lignite/refuse derived fuel blend because refuse derived fuel has lower moisture content than all considered biomass fuels. At a 30% co-firing ratio, both energy and exergy losses decrease by about 20% with respect to base coal for the lignite/refuse derived fuel blend.

Table 16.15. Effect of co-firing on energy losses and external exergy losses for bituminous coal/biomass blends based on a fixed heat input to the steam cycle.

Fuel blend	Co-firing share [%]		Energy loss rate [MW]					Exergy loss rate [MW]			
	P_c	P_b	M	FG	Ash	$\dot{Q}$	$\dot{Q}_{cond}$	M	FG	Ash	$\dot{E}x_h$
Base	100	0	1.237	1.630	0.021	0.850	14.52	1.319	2.469	0.013	0.070
B/RH	90.45	9.55	1.338	1.631	0.024	0.852	14.52	1.427	2.472	0.015	0.070
	81.77	18.23	1.44	1.632	0.028	0.855	14.52	1.536	2.477	0.017	0.070
	73.85	26.15	1.542	1.633	0.032	0.857	14.52	1.644	2.482	0.019	0.070
	66.59	33.41	1.644	1.634	0.035	0.860	14.52	1.753	2.487	0.021	0.070
	59.91	40.09	1.746	1.635	0.039	0.863	14.52	1.862	2.491	0.023	0.070
B/SD	53.76	46.24	1.848	1.636	0.044	0.865	14.52	1.971	2.496	0.026	0.070
	91.63	8.37	1.384	1.628	0.021	0.852	14.52	1.476	2.468	0.013	0.070
	83.84	16.16	1.533	1.627	0.020	0.855	14.52	1.635	2.469	0.013	0.070
	76.56	23.44	1.681	1.626	0.020	0.857	14.52	1.793	2.469	0.013	0.070
	69.74	30.26	1.83	1.625	0.019	0.859	14.52	1.952	2.469	0.013	0.070
B/CL	63.36	36.64	1.979	1.624	0.019	0.862	14.52	2.110	2.470	0.013	0.070
	57.35	42.65	2.127	1.623	0.018	0.864	14.52	2.269	2.470	0.012	0.070
	89.97	10.03	1.330	1.636	0.029	0.852	14.52	1.419	2.479	0.018	0.070
	80.95	19.05	1.424	1.643	0.037	0.855	14.52	1.519	2.490	0.025	0.070
	72.79	27.21	1.519	1.650	0.046	0.858	14.52	1.620	2.502	0.032	0.070
B/RDF	65.37	34.63	1.613	1.657	0.055	0.861	14.52	1.721	2.514	0.040	0.070
	58.60	41.40	1.708	1.664	0.065	0.863	14.52	1.822	2.526	0.048	0.070
	52.40	47.60	1.803	1.671	0.075	0.866	14.52	1.922	2.538	0.058	0.070
	91.38	8.62	1.234	1.624	0.026	0.852	14.52	1.317	2.461	0.016	0.070
	83.40	16.60	1.232	1.618	0.031	0.854	14.52	1.314	2.455	0.019	0.070
	75.97	24.03	1.23	1.613	0.036	0.856	14.52	1.312	2.449	0.022	0.070
	69.05	30.95	1.228	1.607	0.041	0.858	14.52	1.310	2.443	0.025	0.070
	62.59	37.41	1.226	1.601	0.047	0.861	14.52	1.307	2.437	0.028	0.070
	56.55	43.45	1.224	1.596	0.053	0.863	14.52	1.305	2.431	0.032	0.070

Energy and exergy losses with stack gas decrease with increasing biomass content for all lignite/biomass blends due to decrease in furnace exit gas temperature and overall mass flow rate of flue gases. With respect to base coal, the energy loss with exhaust gas decreases by 8.09, 5.33, 7.73, and 7.46% for blends of lignite/rice husk, lignite/sawdust, lignite/chicken litter, and lignite/refuse derived fuel, at a 30% co-firing ratio. Likewise, the exergy loss with flue gases decreases by 8.04, 5.39, 8.09, and 7.46% for blends of lignite/rice husk, lignite/sawdust, lignite/chicken litter, and lignite/refuse derived fuel blend, respectively, when the co-firing ratio increases to 30%.

From Tables 16.13 and 16.14, it can be seen that the energy loss due to unburned combustibles, and radiation and convection, decreases with an increase of biomass due to the decrease in energy. With less energy input, less steam is produced. Hence, heat loss from the condenser decreases with an increase of biomass in the blend. In the same way, the exergy loss due to radiation and convection from the boiler exterior surface decreases with an increase in biomass fraction in the blend, due to a notable decrease in exergy input.

Tables 16.15 and 16.16 provide energy and exergy losses for bituminous coal/biomass blends and lignite/biomass blends respectively, based on a fixed heat input to the steam cycle (case 2). It can be observed from these tables that the trends for energy and exergy losses due to ash and moisture are the same as for case 1. Since a larger amount of biomass compared to case 1 is fed to boiler in case 2, the decrease or increase in other losses is observed to be larger than for case 1. For example, in comparison with base coal, the exergy loss due to moisture increases by 49.43 and 4.38% for the bituminous coal/rice husk blend and the lignite/rice husk blend respectively, when the coal flow rate decrease to 0.70 kg/s.

Table 16.16. Effect of co-firing on energy losses and external exergy losses for lignite/biomass blends based on a fixed heat input to the steam cycle.

Fuel blend	Co-firing share [%]		Energy loss rate [MW]						Exergy loss rate [MW]			
	P_c	P_b	M	FG	Ash	$\dot{Q}$	$\dot{Q}_{cond}$	M	FG	Ash	$\dot{E}_{x_h}$	
Base	100	0	1.967	1.126	0.017	0.602	10.01	2.098	1.742	0.010	0.048	
L/RH	93.27	6.73	1.980	1.127	0.019	0.603	10.01	2.112	1.719	0.011	0.048	
	86.74	13.26	1.995	1.128	0.020	0.604	10.01	2.128	1.695	0.012	0.048	
	80.44	19.56	2.010	1.129	0.022	0.605	10.01	2.144	1.672	0.013	0.048	
	74.36	25.64	2.024	1.130	0.024	0.606	10.01	2.159	1.649	0.014	0.048	
	68.50	31.50	2.039	1.131	0.026	0.607	10.01	2.175	1.625	0.015	0.048	
L/SD	62.84	37.16	2.054	1.132	0.028	0.608	10.01	2.190	1.602	0.016	0.048	
	94.12	5.88	2.012	1.125	0.016	0.603	10.01	2.146	1.726	0.010	0.048	
	88.31	11.69	2.059	1.124	0.016	0.604	10.01	2.196	1.710	0.010	0.048	
	82.62	17.38	2.106	1.123	0.015	0.605	10.01	2.246	1.695	0.009	0.048	
	77.03	22.97	2.153	1.122	0.014	0.606	10.01	2.296	1.679	0.009	0.048	
L/CL	71.54	28.46	2.200	1.121	0.013	0.606	10.01	2.346	1.664	0.009	0.048	
	66.16	33.84	2.246	1.120	0.013	0.607	10.01	2.396	1.648	0.008	0.048	
	92.92	7.08	1.975	1.130	0.022	0.603	10.01	2.107	1.718	0.014	0.048	
	86.10	13.90	1.984	1.135	0.026	0.604	10.01	2.117	1.695	0.017	0.048	
	79.57	20.43	1.994	1.139	0.031	0.605	10.01	2.127	1.671	0.021	0.048	
L/RDF	73.31	26.69	2.003	1.144	0.036	0.606	10.01	2.137	1.648	0.025	0.048	
	67.32	32.68	2.012	1.149	0.041	0.607	10.01	2.147	1.625	0.030	0.048	
	61.56	38.44	2.022	1.153	0.047	0.608	10.01	2.156	1.601	0.034	0.048	
	93.95	6.05	1.909	1.121	0.020	0.603	10.01	2.036	1.720	0.012	0.048	
	87.99	12.01	1.852	1.117	0.022	0.603	10.01	1.975	1.698	0.014	0.048	
	82.16	17.84	1.795	1.113	0.025	0.604	10.01	1.914	1.677	0.015	0.048	
	76.46	23.54	1.738	1.109	0.028	0.605	10.01	1.853	1.655	0.017	0.048	
	70.89	29.11	1.680	1.105	0.031	0.605	10.01	1.792	1.633	0.018	0.048	
	65.44	34.56	1.623	1.101	0.034	0.606	10.01	1.731	1.612	0.020	0.048	

Regarding energy and exergy losses through the stack, it was found from the composition of flue gases that the net flue gas mass flow rate increases for rice husk and chicken litter blends and decreases for sawdust and refuse derived fuel blends, with an increase of biomass in the blend. As a result, energy and exergy losses with flue gases increase for rice husk and chicken litter blends, and decrease for sawdust and refuse derived fuel blends.

Energy losses due to unburned combustibles as well as radiation and convection slightly increase as the energy input increases. However, the exergy loss from the boiler exterior surface remains roughly the same at all co-firing ratios for all blends because the increase in heat loss through radiation and convection is offset by a decrease in furnace exterior wall temperature.

16.7.2.3 Effect of co-firing on irreversibilities

The irreversibility of system components for bituminous coal/biomass blends at different co-firing ratios are shown in Table 16.17 for a fixed fuel input to the boiler. The largest exergy destruction occurs in the boiler, and is attributable to chemical reaction and heat transfer across a large temperature difference between the product gas and the feed water. For 100% coal firing, 38.70% of the exergy supplied is destroyed due to irreversibilities in the boiler, and 23.31% of this value is destroyed in the combustor only. The greatest exergy destruction in the steam cycle occurs in the condenser. In fact, the irreversibility rate of the condenser is greater than that of the heat exchanger and accounts for 32.64% of total plant exergy destruction. The overall plant exergy destruction is determined to be 68.80% of the exergy input.

It can be seen from Table 16.17 that the irreversibility rates of all components and the overall plant decrease with increasing biomass content in the fuel blend. As the percent share of biomass

Table 16.17. Effect of co-firing on irreversibilities in components for bituminous coal/biomass blends based on a fixed fuel flow rate¹.

Fuel blend	Co-firing share [%]		Irreversibility rate [MW]							
	P_c	P_b	$\dot{I}_c$	$\dot{I}_{rs}$	$\dot{I}_b$	$\dot{I}_{cond}$	$\dot{I}_{HPT}$	$\dot{I}_{LPT}$	$\dot{I}_{FWH}$	$\dot{I}_t$
Base	100	0	8.20	4.52	12.72	6.58	0.25	1.14	0.821	21.51
B/RH	95	5	8.09	4.39	12.48	6.42	0.24	1.11	0.801	21.06
	90	10	7.97	4.27	12.24	6.25	0.23	1.08	0.780	20.59
	85	15	7.84	4.15	11.99	6.09	0.23	1.05	0.760	20.14
	80	20	7.73	4.02	11.75	5.92	0.22	1.03	0.739	19.67
	75	25	7.60	3.91	11.51	5.76	0.22	1.00	0.719	19.22
	70	30	7.48	3.79	11.27	5.59	0.21	0.97	0.697	18.73
B/SD	95	5	8.13	4.41	12.55	6.43	0.24	1.12	0.804	21.15
	90	10	8.06	4.30	12.37	6.31	0.24	1.09	0.787	20.81
	85	15	7.99	4.20	12.20	6.17	0.23	1.07	0.769	20.45
	80	20	7.91	4.10	12.02	6.03	0.23	1.04	0.752	20.08
	75	25	7.85	3.99	11.85	5.89	0.22	1.02	0.734	19.72
	70	30	7.77	3.89	11.67	5.75	0.22	0.99	0.717	19.35
B/CL	95	5	8.05	4.38	12.43	6.41	0.24	1.11	0.800	20.99
	90	10	7.87	4.26	12.13	6.24	0.23	1.08	0.778	20.47
	85	15	7.71	4.12	11.83	6.07	0.23	1.05	0.757	19.95
	80	20	7.56	3.98	11.53	5.89	0.22	1.02	0.734	19.40
	75	25	7.39	3.85	11.24	5.72	0.21	0.99	0.713	18.88
	70	30	7.22	3.72	10.94	5.54	0.21	0.96	0.692	18.35
B/RDF	95	5	8.10	4.42	12.52	6.44	0.24	1.11	0.803	21.14
	90	10	8.02	4.31	12.33	6.29	0.24	1.09	0.785	20.74
	85	15	7.92	4.21	12.13	6.14	0.23	1.06	0.767	20.33
	80	20	7.82	4.11	11.93	6.00	0.23	1.04	0.749	19.95
	75	25	7.73	4.00	11.73	5.86	0.22	1.01	0.731	19.55
	70	30	7.63	3.90	11.53	5.69	0.21	0.99	0.713	19.15

¹ $\dot{I}_c, \dot{I}_{rs}, \dot{I}_{cond}, \dot{I}_{HPT}, \dot{I}_{LPT}, \dot{I}_{cond}, \dot{I}_{FWH}$, and $\dot{I}_t$ are irreversibility rates of combustion chamber, heat exchanger (reheater and superheater), boiler, high pressure turbine, low pressure turbine, condenser, feed water heater, and total plant, respectively.

co-firing increases, the exergy input to the plant decreases; hence less exergy is destroyed in the combustor. Moreover, the exergy of the product gas decreases because the furnace exit gas temperature decreases. The irreversibility rate of the heat exchanger decreases because a lower temperature product gas decreases the temperature difference between the feed water and the product gas. As a result, irreversibility rate of the boiler decreases. Since the steam cycle conditions are fixed, the irreversibility rate of all other components decreases because of the lower exergy input to the cycle.

Among the bituminous coal/biomass blends, the largest decrease in irreversibility rate occurs for the bituminous coal/chicken litter blend because the decrease in furnace exit gas temperature with increasing chicken litter content is the largest for this blend. As a result, the decrease in the irreversibility rate of the heat exchanger is the highest at all co-firing ratios for this blend. Further, the exergy carried by this blend at all co-firing ratios is the smallest compared to other blends. Therefore, less exergy is destroyed in the combustion chamber. For this blend, every 5% addition of chicken litter decreases the boiler and, hence, the plant irreversibility rate by roughly 3%. In contrast, the lowest decrease in irreversibility rate occurs for the bituminous coal/sawdust blend because the largest amount of exergy is destroyed in the combustion chamber for this blend. At all co-firing ratios, the irreversibility rate of the heat exchanger decreases more for the bituminous coal/sawdust blend than for the bituminous coal/refuse derived fuel blend because the product gas temperature decreases more for the bituminous coal/sawdust blend than the

Table 16.18. Effect of co-firing on irreversibilities in components for lignite/biomass blends based on a fixed fuel flow rate.

Fuel blend	Co-firing share [%]		Irreversibility rate [MW]							
	P_c	P_b	$\dot{I}_c$	$\dot{I}_{rs}$	$\dot{I}_b$	$\dot{I}_{cond}$	$\dot{I}_{HPT}$	$\dot{I}_{LPT}$	$\dot{I}_{FWH}$	$\dot{I}_t$
Base	100	0	6.51	3.01	9.52	4.54	0.17	0.79	0.57	15.59
L/RH	95	5	6.48	2.96	9.44	4.48	0.17	0.77	0.56	15.42
	90	10	6.43	2.92	9.35	4.41	0.17	0.76	0.55	15.25
	85	15	6.40	2.87	9.27	4.35	0.16	0.75	0.54	15.09
	80	20	6.37	2.82	9.19	4.29	0.16	0.74	0.54	14.92
	75	25	6.33	2.77	9.11	4.23	0.16	0.73	0.53	14.75
	70	30	6.29	2.74	9.02	4.16	0.16	0.72	0.52	14.59
L/SD	95	5	6.50	2.99	9.49	4.50	0.17	0.78	0.56	15.51
	90	10	6.47	2.96	9.43	4.47	0.17	0.77	0.56	15.47
	85	15	6.42	2.93	9.35	4.43	0.17	0.77	0.55	15.40
	80	20	6.39	2.90	9.27	4.39	0.16	0.76	0.55	15.32
	75	25	6.36	2.88	9.24	4.35	0.16	0.75	0.54	15.25
	70	30	6.28	2.85	9.13	4.32	0.16	0.75	0.54	15.21
L/CL	95	5	6.43	2.95	9.38	4.47	0.17	0.77	0.56	15.36
	90	10	6.35	2.90	9.25	4.40	0.16	0.76	0.55	15.12
	85	15	6.28	2.83	9.11	4.33	0.16	0.75	0.54	14.90
	80	20	6.19	2.78	8.97	4.26	0.16	0.74	0.53	14.67
	75	25	6.12	2.72	8.83	4.18	0.16	0.72	0.52	14.42
	70	30	6.03	2.67	8.70	4.11	0.15	0.71	0.51	14.19
L/RDF	95	5	6.50	2.98	9.48	4.50	0.17	0.78	0.56	15.50
	90	10	6.49	2.95	9.44	4.45	0.17	0.77	0.56	15.39
	85	15	6.47	2.93	9.40	4.41	0.17	0.76	0.55	15.31
	80	20	6.46	2.90	9.36	4.37	0.16	0.76	0.54	15.20
	75	25	6.45	2.87	9.32	4.30	0.16	0.75	0.54	15.09
	70	30	6.44	2.84	9.28	4.28	0.16	0.74	0.53	15.00

bituminous coal/refuse derived fuel blend. However, due to relatively larger exergy destruction in the combustor for the bituminous coal/sawdust blend than the bituminous coal/refuse derived fuel blend, the overall irreversibility rate of the boiler is larger for the bituminous coal/sawdust blend than for the bituminous coal/refuse derived fuel blend, and in fact is the largest among all blends. For this blend, every 5% addition of sawdust causes the boiler and hence overall plant irreversibility rate to decrease by about 1.60%. Similarly, the decrease in irreversibility rate for the bituminous coal/rice husk blend is greater than for the bituminous coal/refuse derived fuel blend because the furnace exit gas temperature decreases more for the bituminous coal/rice husk blend than the bituminous coal/refuse derived fuel blend, as the biomass in the blend increases.

Table 16.18 illustrates the effect of co-firing on the irreversibilities of components based on a fixed fuel flow when lignite is used as base coal.

It is evident from Table 16.18 that the boiler is the major source of exergy destruction. It is also noted that the condenser irreversibility rate is greater than that of the combustor and the heat exchanger. For 100% lignite firing, the total exergy destruction rate occurring in the boiler is 34.89% of the exergy input rate, out of which 20.65% occurs in the combustor and 14.24% in the heat exchanger. The total irreversibility rate of the plant is found to be 63.47% of the exergy input rate.

Similar trends in irreversibility rate are observed as were found for bituminous coal and biomass co-firing when lignite is used. That is, the irreversibility rates of all components and the plant decrease as the co-firing share increases. With increasing biomass content, the largest decrease in irreversibility rate occurs for the lignite/chicken litter blend because the largest decrease in

Table 16.19. Effect of co-firing on irreversibilities in components for bituminous coal/biomass blends based on a fixed heat input to the steam cycle.

Fuel blend	Co-firing share [%]		Irreversibility rate [MW]							
	P_c	P_b	$\dot{I}_c$	$\dot{I}_{rs}$	$\dot{I}_b$	$\dot{I}_{cond}$	$\dot{I}_{HPT}$	$\dot{I}_{LPT}$	$\dot{I}_{FWH}$	$\dot{I}_t$
Base	100	0	8.20	4.52	12.72	6.58	0.25	1.14	0.821	21.51
B/RH	90.45	9.55	8.38	4.49	12.88	6.58	0.25	1.14	0.82	21.67
	81.77	18.23	8.55	4.48	13.03	6.58	0.25	1.14	0.82	21.82
	73.85	26.15	8.72	4.46	13.18	6.58	0.25	1.14	0.82	21.98
	66.59	33.41	8.98	4.43	13.34	6.58	0.25	1.14	0.82	22.13
	59.91	40.09	9.07	4.41	13.49	6.58	0.25	1.14	0.82	22.28
B/SD	53.76	46.24	9.25	4.40	13.65	6.58	0.25	1.14	0.82	22.44
	91.63	8.37	8.40	4.49	12.89	6.58	0.25	1.14	0.82	21.68
	83.84	16.16	8.56	4.49	13.05	6.58	0.25	1.14	0.82	21.84
	76.56	23.44	8.75	4.47	13.22	6.58	0.25	1.14	0.82	22.01
	69.74	30.26	8.92	4.46	13.38	6.58	0.25	1.14	0.82	22.17
B/CL	63.36	36.64	9.09	4.45	13.54	6.58	0.25	1.14	0.82	22.34
	57.35	42.65	9.26	4.44	13.71	6.58	0.25	1.14	0.82	22.50
	89.97	10.03	8.33	4.47	12.81	6.58	0.25	1.14	0.82	21.60
	80.95	19.05	8.45	4.44	12.89	6.58	0.25	1.14	0.82	21.68
	72.79	27.21	8.54	4.42	12.97	6.58	0.25	1.14	0.82	21.76
B/RDF	65.37	34.63	8.66	4.39	13.05	6.58	0.25	1.14	0.82	21.85
	58.60	41.40	8.78	4.35	13.14	6.58	0.25	1.14	0.82	21.93
	52.40	47.60	8.89	4.32	13.22	6.58	0.25	1.14	0.82	22.01
	91.38	8.62	8.37	4.50	12.87	6.58	0.25	1.14	0.82	21.66
	83.40	16.60	8.52	4.50	13.02	6.58	0.25	1.14	0.82	21.81
	75.97	24.03	8.68	4.49	13.17	6.58	0.25	1.14	0.82	21.96
	69.05	30.95	8.83	4.48	13.32	6.58	0.25	1.14	0.82	22.11
	62.59	37.41	8.99	4.47	13.46	6.58	0.25	1.14	0.82	22.26
	56.55	43.45	9.14	4.47	13.61	6.58	0.25	1.14	0.82	22.40

furnace exit gas temperature takes place for this blend. In addition, the exergy carried by this blend at all co-firing ratios is the smallest compared to other blends. Every 5% addition of chicken litter decreases the system irreversibility rate by about 1.6%. In contrast, the lowest decrease in irreversibility rate with the addition of biomass occurs for the lignite/sawdust blend. Similarly, the irreversibility rate for the lignite/rice husk blend decreases more than for the lignite/refuse derived fuel blend.

Tables 16.19 and 16.20 list the component irreversibilities for bituminous coal/biomass blends and lignite/biomass blends respectively, when the system operates with fixed heat input to steam cycle.

Since the temperatures and pressures of the steam cycle components are fixed in case 2, the useful exergy transferred to the cycle with respect to bituminous coal/biomass blends and lignite/biomass blends is same for all co-firing ratios. Therefore, the irreversibility rate of the turbines, pumps, feed water heater, and condenser are not changing. However, the irreversibility rate of the boiler subsystem increases due to the temperature changes and the varying fuel consumption. Furthermore, the irreversibility rate of the combustor increases and that of heat exchanger decreases with increasing biomass content for all blends. Due to a larger fuel consumption than for case 1, the exergy input to the combustor increases. Since the exergy input to the steam cycle is fixed, only a fixed amount of exergy is transferred between the feed water and the product gas, and the rest is destroyed in the combustion chamber. The irreversibility rate of the combustor increases due to a decrease in the product gas temperature; consequently, the exergy of the product gas decreases. The irreversibility rate of the heat exchanger decreases because a lower furnace exit gas temperature decreases the temperature difference between the product gas and

Table 16.20. Effect of co-firing on irreversibilities in components for lignite/biomass blends based on a fixed heat input to the steam cycle.

Fuel blend	Co-firing share [%]		Irreversibility rate [MW]							
	P_c	P_b	$\dot{I}_c$	$\dot{I}_{rs}$	$\dot{I}_b$	$\dot{I}_{cond}$	$\dot{I}_{HPT}$	$\dot{I}_{LPT}$	$\dot{I}_{FWH}$	$\dot{I}_t$
Base	100	0	6.51	3.01	9.52	4.54	0.17	0.79	0.57	15.59
L/RH	93.27	6.73	6.59	3.00	9.59	4.54	0.17	0.79	0.57	15.65
	86.74	13.26	6.67	2.99	9.66	4.54	0.17	0.79	0.57	15.72
	80.44	19.56	6.74	2.98	9.72	4.54	0.17	0.79	0.57	15.79
	74.36	25.64	6.80	2.99	9.79	4.54	0.17	0.79	0.57	15.85
	68.50	31.50	6.88	2.98	9.86	4.54	0.17	0.79	0.57	15.92
L/SD	62.84	37.16	6.96	2.97	9.92	4.54	0.17	0.79	0.57	15.99
	94.12	5.88	6.59	3.01	9.60	4.54	0.17	0.79	0.57	15.66
	88.31	11.69	6.67	3.00	9.67	4.54	0.17	0.79	0.57	15.74
	82.62	17.38	6.75	3.00	9.75	4.54	0.17	0.79	0.57	15.81
	77.03	22.97	6.82	3.00	9.82	4.54	0.17	0.79	0.57	15.89
L/CL	71.54	28.46	6.90	3.00	9.90	4.54	0.17	0.79	0.57	15.96
	66.16	33.84	6.98	2.99	9.97	4.54	0.17	0.79	0.57	16.03
	92.92	7.08	6.55	2.99	9.54	4.54	0.17	0.79	0.57	15.60
	86.10	13.90	6.58	2.98	9.56	4.54	0.17	0.79	0.57	15.62
	79.57	20.43	6.61	2.96	9.58	4.54	0.17	0.79	0.57	15.64
L/RDF	73.31	26.69	6.65	2.95	9.60	4.54	0.17	0.79	0.57	15.66
	67.32	32.68	6.68	2.93	9.61	4.54	0.17	0.79	0.57	15.68
	61.56	38.44	6.71	2.92	9.63	4.54	0.17	0.79	0.57	15.70
	93.95	6.05	6.58	3.01	9.59	4.54	0.17	0.79	0.57	15.65
	87.99	12.01	6.64	3.01	9.65	4.54	0.17	0.79	0.57	15.71
	82.16	17.84	6.70	3.01	9.71	4.54	0.17	0.79	0.57	15.78
	76.46	23.54	6.77	3.01	9.77	4.54	0.17	0.79	0.57	15.84
	70.89	29.11	6.82	3.02	9.84	4.54	0.17	0.79	0.57	15.90
	65.44	34.56	6.89	3.01	9.90	4.54	0.17	0.79	0.57	15.97

the feed water heater. Note that the decrease in the irreversibility rate of the heat exchanger is smaller than the increase in irreversibility rate of the combustor, which results in an increase in the overall irreversibility rate of the boiler, and of the plant. Like case 1, relative to other blends, the irreversibility rate of the boiler and hence the overall plant is the largest for sawdust blends and the smallest for chicken litter blends, at all co-firing ratios.

16.7.3 Effect of co-firing on efficiencies

16.7.3.1 Boiler energy efficiency

The effect of co-firing on boiler energy efficiency based on a fixed fuel flow is shown in Figure 16.9. It can be seen that boiler energy efficiency decreases as the biomass proportion increases. For all blends, the efficiency decreases by less than 1% with respect to the base coal case, at a 30% co-firing ratio. The reduction in efficiency is mainly attributable to the heating value, moisture content, and ash content of biomass. It is also observed that the greatest efficiency reductions occur for the coal/chicken litter blends. This observation is due to the fact that the greatest reductions in furnace exit gas temperature occur for chicken litter blends, reducing the heat transfer rate between the product gas and feed water compared to other blends, as pointed out in section 16.6.1. When the co-firing ratio increases from 0 to 30%, the boiler energy efficiency decreases from 87.01 to 86.06% for the bituminous coal/chicken litter blend and from 84.70 to 84.01% for the lignite/chicken litter blend. In contrast, the energy efficiency reduction is the smallest for refuse derived fuel blends because they exhibit the lowest furnace exit gas

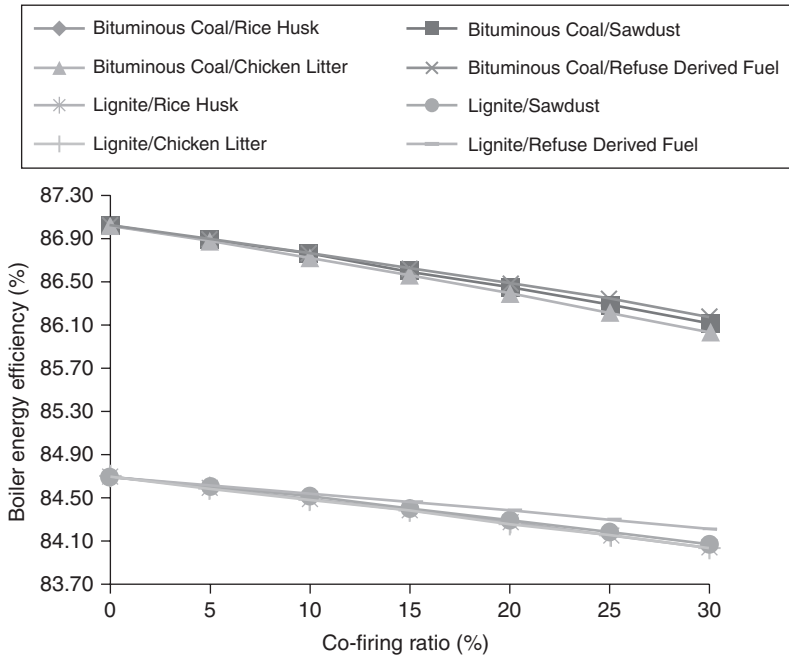


Figure 16.9. Effect of co-firing on boiler energy efficiency based on a fixed fuel flow rate.

temperature decreases. At a 30% co-firing ratio, the boiler energy efficiency decreases to 86.18% and 84.19% for blends of bituminous coal/refuse derived fuel and lignite/refuse derived fuel, respectively.

The effect of co-firing on boiler energy efficiency is shown in Figure 16.10 based on a fixed steam input to the steam cycle. The trends are similar to those for case 1, except that the efficiency decreases more than for case 1 because of the increased fuel input to boiler with increasing biomass proportion. The decreases in boiler energy efficiency are the greatest for chicken litter blends and the lowest for refuse derived fuel blends. Relative to base coal, the boiler energy efficiency drops to 85.38 and 83.83% for blends of bituminous coal/chicken litter and lignite/chicken litter, respectively, when the coal mass flow rate decreases to 0.70 kg/s. Similarly, the boiler energy efficiency drops to 85.71% for the bituminous coal/refuse derived fuel blend and 84.15% for the lignite/refuse derived fuel blend, for a coal input rate of 0.70 kg/s.

16.7.3.2 Plant energy efficiency

Figures 16.11 and 16.12 illustrate that the overall plant energy efficiency also decreases as the biomass proportion increases. The trends are similar as those observed for the boiler energy efficiency. For a fixed fuel flow, the plant energy efficiency decreases from 35.02 to 34.65, 34.66, 34.61, and 34.69% for blends of bituminous coal/rice husk, bituminous coal/sawdust, bituminous coal/chicken litter, and bituminous coal/refuse derived fuel respectively, when the co-firing ratio increase from 0 to 30%. Similarly, the plant energy efficiency decrease from 34.08% for the base coal case to 33.82, 33.85, 33.79, and 33.88%, respectively, for blends of lignite/rice husk, lignite/sawdust, lignite/chicken litter, and lignite/refuse derived fuel, at a 30% co-firing ratio.

The efficiency drops are greater in case of a fixed heat input to cycle than in case of a fixed fuel flow. For a coal input rate of 0.70 kg/s, the plant energy efficiency decreases to 34.40, 34.43, 34.35, and 34.49%, respectively, for blends of bituminous coal/rice husk, bituminous

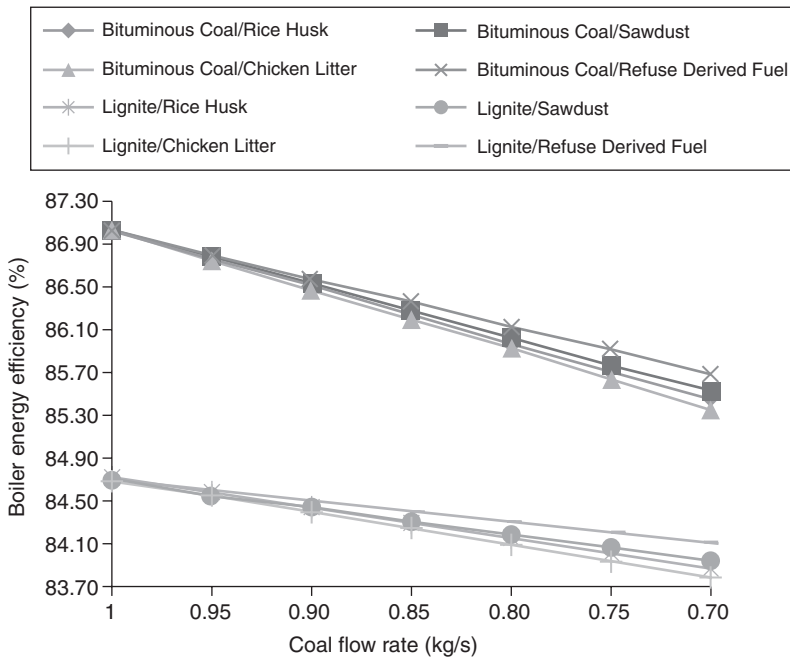


Figure 16.10. Effect of co-firing on boiler energy efficiency based on a fixed heat input to the steam cycle.

coal/sawdust, bituminous coal/chicken litter, and bituminous coal/refuse derived fuel. Similarly, the plant energy efficiency decreases to 33.76, 33.79, 33.73, and 33.86% respectively for blends of lignite/rice husk, lignite/sawdust, lignite/chicken litter, and lignite/refuse derived fuel, when the coal flow rate decreases to 0.70 kg/s.

16.7.3.3 Boiler exergy efficiency

The boiler exergy efficiency also decreases with increasing biomass content in the blend (see Figs 16.13 and 16.14). At all co-firing ratios, the greatest reductions in boiler exergy efficiency occur for sawdust blends, while the smallest reductions occur for chicken litter blends. Correspondingly, sawdust blends exhibit the largest exergy losses at all co-firing ratios compared to other blends. In contrast, chicken litter blends exhibit the smallest exergy losses at all co-firing ratios compared to other blends, so the reductions in boiler exergy efficiency are the smallest for those blends. Similarly, the reductions in boiler exergy efficiency are greater for rice husk blends than for refuse derived fuel blends. In the case of a fixed fuel flow, the boiler exergy efficiency decreases from 46.89 to 45.88% for bituminous coal/chicken litter blend and from 44.67 to 44.41% for lignite/chicken litter blend, when the co-firing ratio increases from 0 to 30%. The boiler exergy efficiency decreases to 45.67 and 43.73% for blends of bituminous coal/sawdust and lignite/sawdust, respectively, at a 30% co-firing ratio.

It can be observed from Figures 16.13 and 16.14 that for all blends the boiler exergy efficiency decreases more for the case of a fixed heat input to the steam cycle than for the case of a fixed fuel flow. When the coal flow rate declines from 1.00 kg/s to 0.70 kg/s, the boiler exergy efficiency decreases to 45.15, 45.06, 45.83, and 45.34% for blends of bituminous coal/rice husk, bituminous coal/sawdust, bituminous coal/chicken litter, and bituminous coal/refuse derived fuel, respectively. Correspondingly, the boiler exergy efficiency decreases from 44.67 to 43.70, 43.61, 44.32, and 43.87% for blends of lignite/rice husk, lignite/sawdust, lignite/chicken litter, and lignite/refuse derived fuel, respectively.

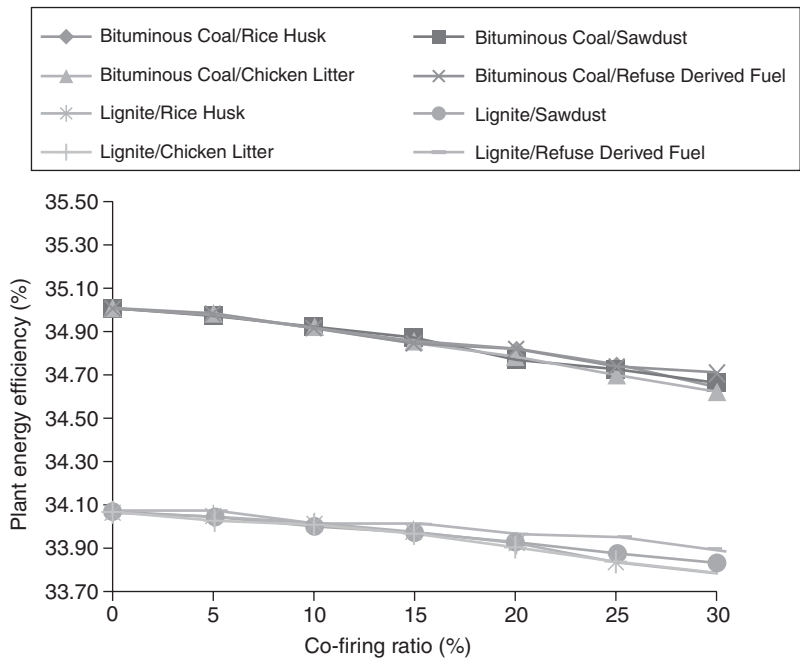


Figure 16.11. Effect of co-firing on plant energy efficiency based on a fixed fuel flow rate.

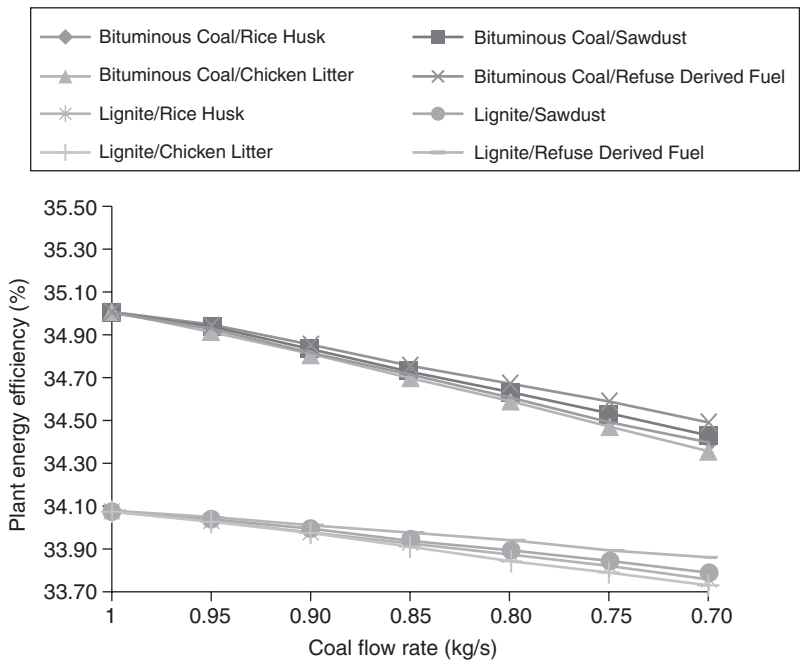


Figure 16.12. Effect of co-firing on plant energy efficiency based on a fixed heat input to the steam cycle.

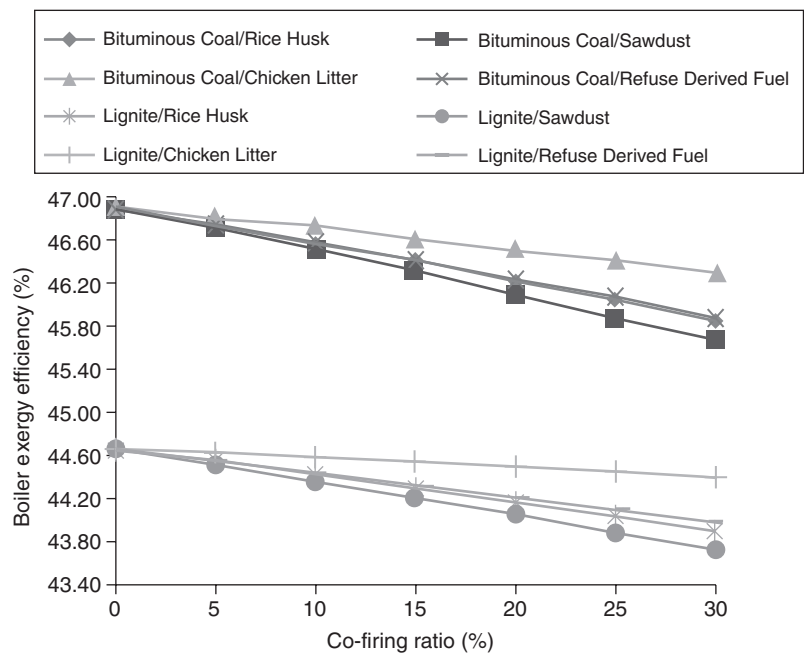


Figure 16.13. Effect of co-firing on boiler exergy efficiency based on a fixed fuel flow rate.

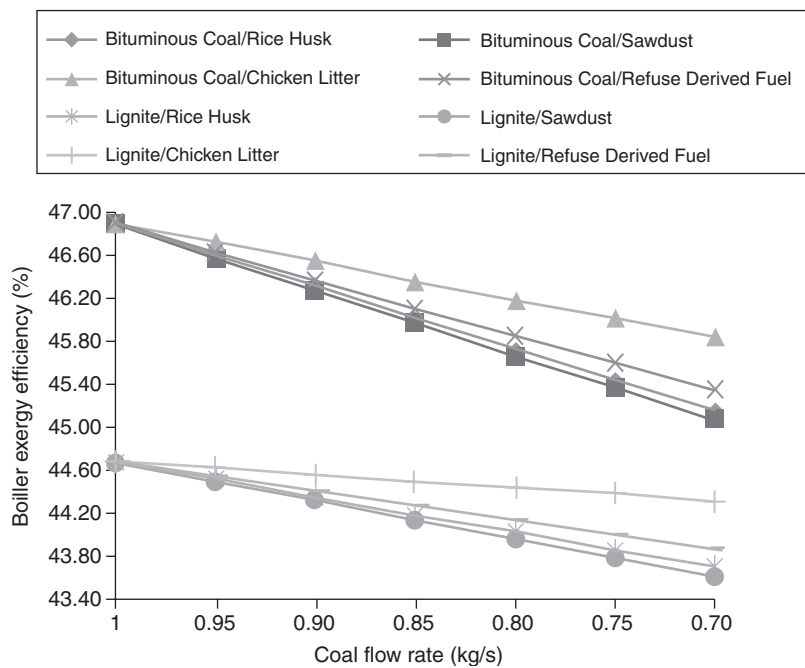


Figure 16.14. Effect of co-firing on boiler exergy efficiency based on a fixed heat input to the steam cycle.

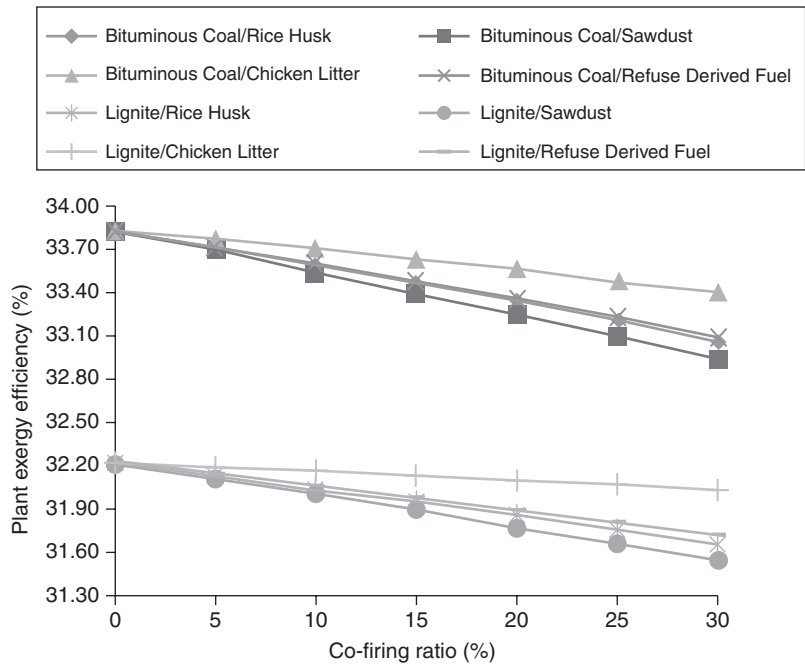


Figure 16.15. Effect of co-firing on plant exergy efficiency based on a fixed fuel flow rate.

16.7.3.4 Plant exergy efficiency

Plant exergy efficiencies for all blends for case 1 are compared in Figure 16.15. The trends are similar to those for the boiler exergy efficiency. The plant exergy efficiency decreases the least for chicken litter blends and the most for sawdust blends. When the co-firing ratio increases from 0% to 30%, the plant exergy efficiency declines from 33.82 to 33.07, 32.94, 33.39, and 33.09% for blends of bituminous coal/rice husk, bituminous coal/sawdust, bituminous coal/chicken litter, and bituminous coal/refuse derived fuel, respectively. Similarly, the plant exergy efficiency reduces at a 30% co-firing ratio to 31.66, 31.54, 32.03, and 31.72% for blends of lignite/rice husk, lignite/sawdust, lignite/chicken litter, and lignite/refuse derived fuel, respectively.

Plant exergy efficiencies for all blends are compared in Figure 16.16 for case 2. When the coal flow rate decreases to 0.70 kg/s, the plant exergy efficiency reduces to 32.57, 32.50, 33.05, and 33.05%, respectively, for blends of bituminous coal/rice husk, bituminous coal/sawdust, bituminous coal/chicken litter, and bituminous coal/refuse derived fuel. Similarly, the plant exergy efficiency reduces from 32.22 to 31.52, 31.45, 31.97, and 31.64%, respectively, for blends of lignite/rice husk, lignite/sawdust, lignite/chicken litter, and lignite/refuse derived fuel, at a coal input rate of 0.70 kg/s.

16.7.4 Effect of co-firing on emissions

The effect of co-firing on various gaseous emissions is described, using two types of emission factors that represent normalized mass emissions. The emission factors are in energy-based (g/kWh) and mass-based (kg/Mg) units. The energy-based factor represents the mass of emission per unit output (1 kWh) of electrical energy from the overall plant, while the mass-based factor represents the mass of emission per unit mass of fuel input (1 Mg) to the overall plant. Throughout this section, gross (total) and net CO₂ emissions are considered, where the gross emissions include all material exiting the plant stack, while the net emissions are discounted by the CO₂ used in growing

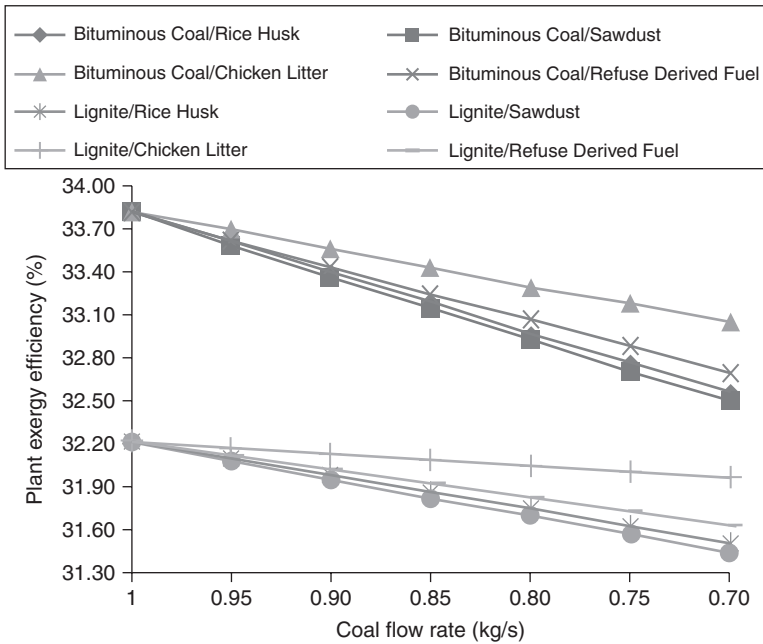


Figure 16.16. Effect of co-firing on plant exergy efficiency based on a fixed heat input to the steam cycle.

biomass and thus take into account the fact that biomass is relatively CO_2 neutral. The mass-based emission factors for all the blends and the two cases considered are shown in Tables 16.21 and 16.22 (with the listing for CO_2 representing gross emissions).

Since biomass fuels have lower carbon fractions than coals, the mass-based CO_2 emission factors decrease for all blends as co-firing ratio increases. The most advantageous biomass in terms of CO_2 emissions reduction is chicken litter because it has the lowest carbon content of the considered biomass fuels. The mass-based CO_2 emission factor decreases by 15.43% for the bituminous coal/chicken litter blend and 9.94% for the lignite/chicken litter blend, as the co-firing ratio rises from 0 to 30%, based on a fixed fuel flow rate. The corresponding mass-based CO_2 emission factor reductions, based on a fixed heat input to the steam cycle, are similar, at 24.52% for the bituminous coal/chicken litter blend and 12.75% for the lignite/chicken litter blend.

The mass-based NO_x emission factor decreases for all bituminous coal/biomass blends except bituminous coal/chicken litter. This is due to that fact that all considered biomass fuels except chicken litter has lower nitrogen concentrations than bituminous coal. Similarly, since all considered biomass fuels except sawdust contain more nitrogen than lignite, the mass-based NO_x emission factor increases for all lignite/biomass blends except lignite/sawdust. Sawdust is the most beneficial biomass for reducing NO_x emissions because of its small nitrogen content. At a 30% co-firing ratio, the mass-based NO_x emission factor declines by 27.78% for the bituminous coal/sawdust blend and 24.14% for the lignite/sawdust blend, for the case of a fixed fuel flow rate. Similarly, for the case of a fixed heat input to the steam cycle, the mass-based NO_x emission factor decreases by 39.48% for the bituminous coal/sawdust blend and 27.05% for the lignite/sawdust blend, when the coal input rate declines from 1.00 to 0.70 kg/s.

We now consider the mass-based SO_x emission factor for co-firing. For the case of bituminous coal and biomass co-firing, this factor decreases for all blends except bituminous coal/chicken litter because all selected biomass fuels except chicken litter have less sulfur content than bituminous coal. However, in case of lignite and biomass co-firing, the mass-based SO_x emission factor decreases for the lignite/rice husk blend and the lignite/sawdust blend, while this factor increases

Table 16.21. Mass-based emission factors for bituminous coal/biomass blends.

Fuel blend	Based on fixed fuel flow rate					Based on fixed heat input to steam cycle				
	Co-firing share [%]		Emission factor [kg/Mg]			Co-firing share [%]		Emission factor [kg/Mg]		
	P _c	P _b	CO ₂	NO _x	SO _x	P _c	P _b	CO ₂	NO _x	SO _x
Base	100	0	2839	10.08	9.03	100	0	2839	10.08	9.03
B/RH	95	5	2773	9.90	8.64	90.45	9.55	2715	9.74	8.30
	90	10	2708	9.72	8.26	81.77	18.23	2600	9.43	7.62
	85	15	2643	9.54	7.87	73.85	26.15	2498	9.14	7.01
	80	20	2578	9.36	7.49	66.59	33.41	2404	8.89	6.46
	75	25	2513	9.18	7.10	59.91	40.09	2316	8.64	5.94
B/SD	70	30	2447	9.00	6.72	53.76	46.24	2236	8.43	5.47
	95	5	2784	9.61	8.58	91.63	8.37	2747	9.30	8.27
	90	10	2729	9.15	8.13	83.84	16.16	2661	8.57	7.57
	85	15	2675	8.68	7.68	76.56	23.44	2583	7.90	6.92
	80	20	2620	8.22	7.22	69.74	30.26	2507	7.26	6.30
B/CL	75	25	2565	7.75	6.77	63.36	36.64	2437	6.66	5.72
	70	30	2510	7.28	6.32	57.35	42.65	2371	6.10	5.18
	95	5	2766	11.23	9.31	89.97	10.03	2692	12.38	9.60
	90	10	2693	12.37	9.60	80.95	19.05	2560	14.44	10.12
	85	15	2620	13.52	9.89	72.79	27.21	2441	16.31	10.59
B/RDF	80	20	2547	14.66	10.18	65.37	34.63	2333	18.01	11.01
	75	25	2474	15.80	10.46	58.60	41.40	2234	19.55	11.40
	70	30	2401	16.95	10.75	52.40	47.60	2143	20.98	11.76
	95	5	2774	9.94	8.94	91.38	8.62	2726	9.84	8.87
	90	10	2709	9.81	8.86	83.40	16.60	2623	9.63	8.74
	85	15	2644	9.67	8.76	75.97	24.03	2526	9.42	8.61
	80	20	2579	9.53	8.68	69.05	30.95	2436	9.23	8.48
	75	25	2514	9.40	8.59	62.59	37.41	2353	9.06	8.37
	70	30	2449	9.26	8.50	56.55	43.45	2274	8.89	8.27

for the lignite/chicken litter blend and the lignite/refuse derived fuel blend. Sawdust is the most advantageous biomass in terms of SO_x reduction. Based on a fixed fuel flow rate, the mass-based SO_x emission factor decreases at a 30% co-firing ratio by 30.01 and 29.83%, respectively, for blends of bituminous coal/sawdust and lignite/sawdust. Similarly, based on a fixed heat input to the steam cycle, corresponding reductions of 42.62 and 33.81%, respectively, are observed for the mass-based SO_x emission factor for blends of bituminous coal/sawdust and lignite/sawdust, when the coal flow rate decreases to 0.70 kg/s.

16.7.4.1 Energy-based CO₂ emission factors

The impact of co-firing on total (gross) CO₂ emissions are illustrated in terms of energy-based emission factors in Figures 16.17 and 16.18. The gross CO₂ energy-based emission factor increases with co-firing ratio for all bituminous coal/biomass blends except bituminous coal/refuse derived fuel. For lignite/biomass blends, the gross CO₂ energy-based emission factor decreases with co-firing ratio for blends of lignite/chicken litter and lignite/refuse derived fuel and increases for blends of lignite/rice husk and lignite/sawdust.

In case of a fixed fuel flow rate, the increase in gross CO₂ emissions is due to the decrease in network output with increasing co-firing ratio, which generally yields higher emissions compared with 100% coal. The decrease in CO₂ emissions with co-firing ratio for blends of bituminous coal/refuse derived fuel, lignite/refuse derived fuel and lignite/chicken litter is due to the relatively low carbon content of refuse derived fuel and chicken litter, which diminishes the work output reduction. The energy-based CO₂ emission factors at a 30% co-firing ratio are 948.1,

Table 16.22. Mass-based emission factors for lignite/biomass blends.

Fuel blend	Based on fixed fuel flow rate					Based on fixed heat input to steam cycle				
	Co-firing share [%]		Emission factor [kg/Mg]			Co-firing share [%]		Emission factor [kg/Mg]		
	P _c	P _b	CO ₂	NO _x	SO _x	P _c	P _b	CO ₂	NO _x	SO _x
Base	100	0	2062	3.77	3.52	100	0	2062	3.77	3.52
L/RH	95	5	2036	3.91	3.41	93.27	6.73	2026	3.95	3.38
	90	10	2009	4.04	3.30	86.74	13.26	1992	4.13	3.23
	85	15	1983	4.18	3.19	80.44	19.56	1959	4.30	3.09
	80	20	1957	4.31	3.08	74.36	25.64	1926	4.47	2.96
	75	25	1930	4.45	2.97	68.50	31.50	1895	4.63	2.83
L/SD	70	30	1904	4.59	2.86	62.84	37.16	1865	4.78	2.70
	95	5	2046	3.62	3.35	94.12	5.88	2042	3.59	3.31
	90	10	2030	3.47	3.17	88.31	11.69	2024	3.41	3.11
	85	15	2014	3.32	3.00	82.62	17.38	2007	3.24	2.91
	80	20	1998	3.17	2.82	77.03	22.97	1989	3.08	2.71
L/CL	75	25	1982	3.01	2.64	71.54	28.46	1971	2.91	2.52
	70	30	1966	2.86	2.47	66.16	33.84	1953	2.75	2.33
	95	5	2027	5.23	4.09	92.92	7.08	2013	5.85	4.32
	90	10	1993	6.69	4.65	86.10	13.90	1966	7.84	5.09
	85	15	1959	8.15	5.21	79.57	20.43	1921	9.75	5.82
L/RDF	80	20	1925	9.61	5.77	73.31	26.69	1879	11.58	6.53
	75	25	1891	11.07	6.33	67.32	32.68	1838	13.32	7.20
	70	30	1857	12.53	6.89	61.56	38.44	1799	15.01	7.84
	95	5	2036	3.95	3.71	93.95	6.05	2029	3.98	3.75
	90	10	2009	4.13	3.90	87.99	12.01	2000	4.20	3.98
	85	15	1983	4.31	4.09	82.16	17.84	1969	4.41	4.19
	80	20	1957	4.48	4.27	76.46	23.54	1938	4.61	4.41
	75	25	1931	4.66	4.46	70.89	29.11	1909	4.81	4.61
	70	30	1905	4.84	4.65	65.44	34.56	1882	5.01	4.82

946.3, 936.6, and 929 g/kWh, respectively, for blends of bituminous coal/rice husk, bituminous coal/sawdust, bituminous coal/chicken litter, and bituminous coal/refuse derived fuel. The corresponding CO₂ emissions factors are 990.8, 986.9, 978.5, and 964.2 g/kWh for blends of lignite/rice husk, lignite/sawdust, lignite/chicken litter, and lignite/refuse derived fuel, respectively.

For the case of a fixed heat input to the steam cycle, the increase in gross CO₂ emissions with co-firing ratio is due to the increased in mass of CO₂ in the flue gases associated with the large biomass use. The gross CO₂ emissions decrease with respect to 100% coal, reaching 927.5, 977.9 and 961.9 g/kWh, respectively, for blends of bituminous coal/refuse derived fuel, lignite/chicken litter, and lignite/refuse derived fuel at a coal feed rate of 0.70 kg/s.

When net CO₂ emissions to the environment are considered, thereby accounting for the fact that biomass is roughly CO₂ neutral, lower CO₂ emissions result from co-firing, as shown in Figure 16.19. The net CO₂ emissions decrease from 934.3 g/kWh for the base coal case to 769.8, 749.2, 776.9 and 753.9 g/kWh, respectively, for blends of bituminous coal/rice husk, bituminous coal/sawdust, bituminous coal/chicken litter, and bituminous coal/refuse derived fuel, at a 30% co-firing ratio. The corresponding net CO₂ emissions for blends of lignite/rice husk, lignite/sawdust, lignite/chicken litter, and lignite/refuse derived fuel are 751.2, 724.5, 760.5, and 730.5 g/kWh, respectively. The results suggest that the most suitable biomass in terms of CO₂ reduction is sawdust due to it having the highest carbon content among the considered biomass fuels.

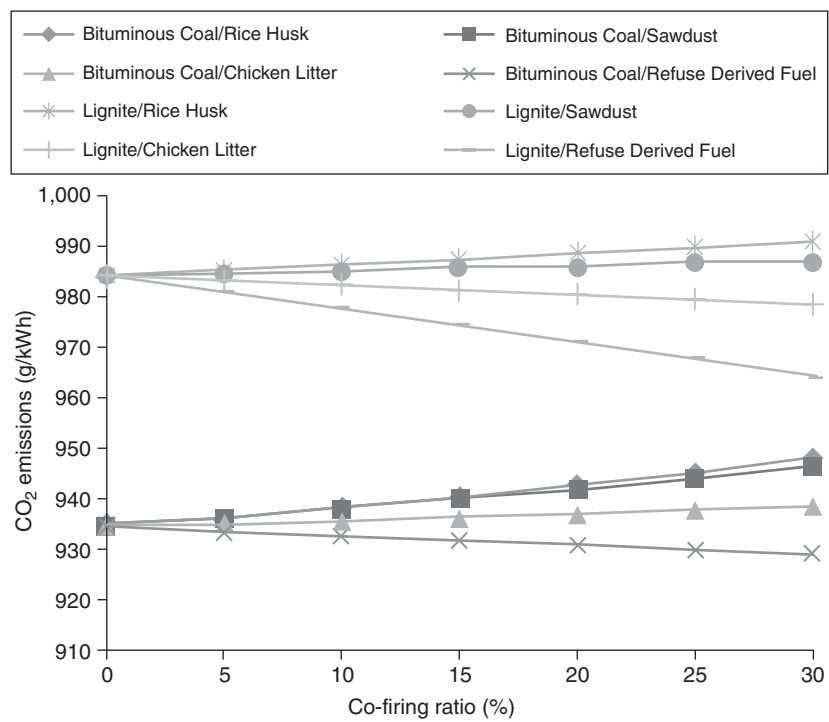


Figure 16.17. Effect of co-firing on gross CO₂ emissions based on a fixed fuel flow rate.

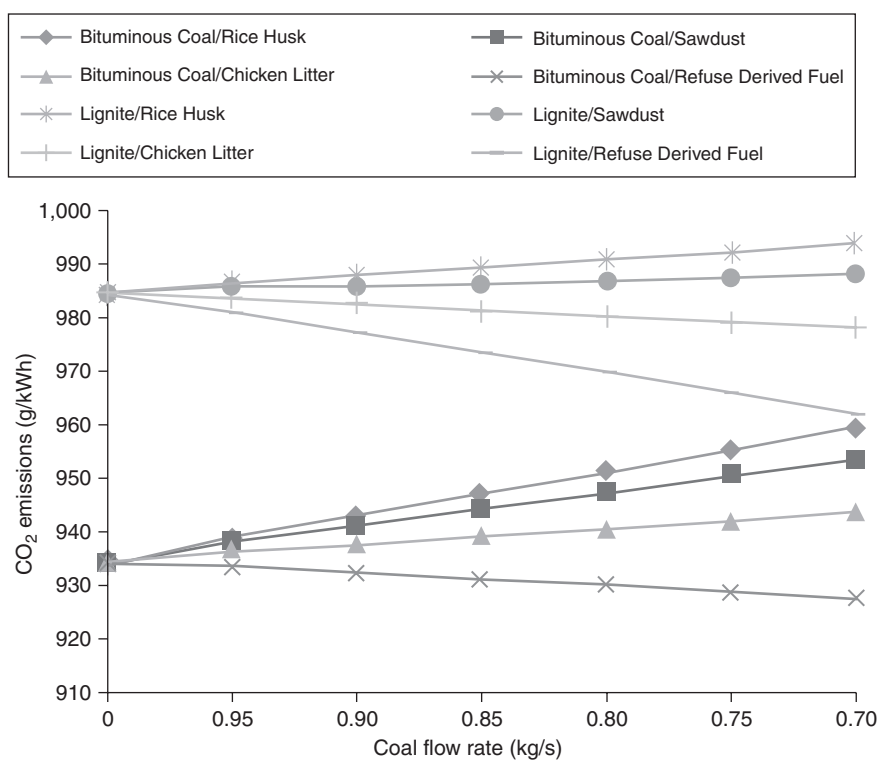


Figure 16.18. Effect of co-firing on gross CO₂ emissions based on a fixed heat input to the steam cycle.

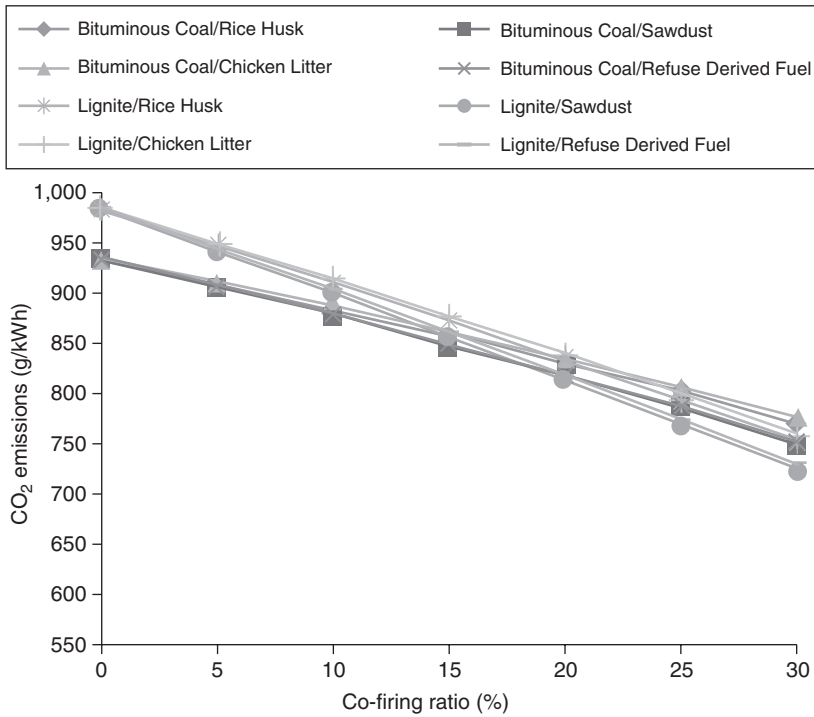


Figure 16.19. Effect of co-firing on net CO₂ emissions based on a fixed fuel flow rate.

The effect of co-firing on net CO₂ emissions based on a fixed heat input to the steam cycle are shown in Figure 16.20. Since the work output of the plant is constant for the case of a fixed heat input to the steam cycle, the net CO₂ emission factors are same for all biomass blends for a given type of coal. At a coal flow rate of 0.70 kg/s, for example, the net CO₂ emission is 654 g/kWh for the bituminous coal/biomass blends and 688.9 g/kWh for the lignite/biomass blends.

16.7.4.2 Energy-based NO_x emission factors

The effect of co-firing on NO_x emissions is illustrated for both cases in Figures 16.21 and 16.22. Since all biomass fuels have higher concentrations of nitrogen than lignite, NO_x emissions increase with co-firing ratio for all lignite/biomass blends except lignite/sawdust. For bituminous coal/biomass blends, however, regardless of the lower nitrogen concentrations of both rice husk and refuse derived fuel relative to bituminous coal, NO_x emissions increase slightly with co-firing ratio for blends of bituminous coal/rice husk and bituminous coal/refuse derived fuel. For the case of a fixed fuel flow rate, the increase in NO_x emissions is due to the decrease in net work output with increasing co-firing ratio, while in the case of a fixed heat input to the steam cycle, the increase in NO_x emissions is due to an increase in the mass of NO_x in flue gases associated with the large biomass use. It is also evident that the most advantageous biomass in terms of NO_x reduction is sawdust because of its very low nitrogen content. For a fixed fuel flow rate, NO_x emissions decrease from 3.32 to 2.75 g/kWh for the bituminous coal/sawdust blend and from 1.80 to 1.44 g/kWh for the lignite/sawdust blend, as the co-firing ratio increases from 0 to 30%. The corresponding NO_x emission at a coal feed rate of 0.70 kg/s, based on a fixed heat input to the steam cycle, is 2.45 g/kWh for the bituminous coal/sawdust blend and 1.44 g/kWh for the lignite/sawdust blend.

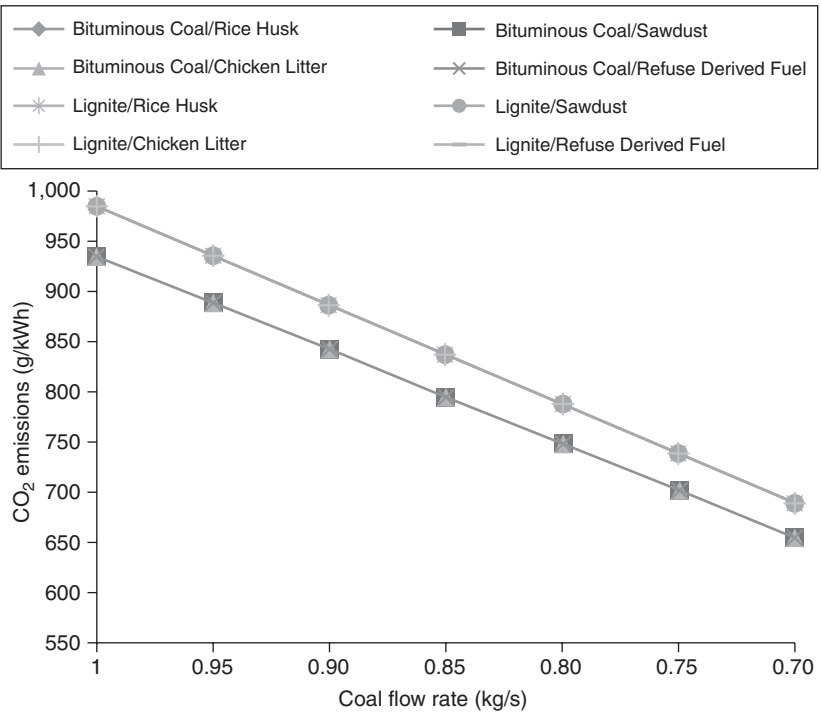


Figure 16.20. Effect of co-firing on net CO₂ emissions based on a fixed heat input to the steam cycle. The upper and bottom lines denote emission factors for lignite/biomass blends and bituminous coal/biomass blends, respectively.

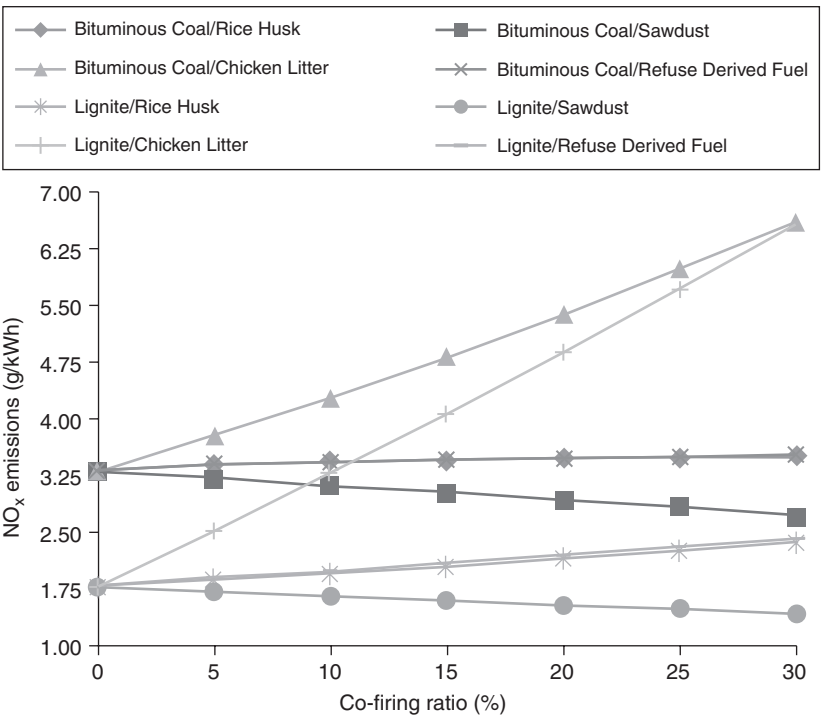


Figure 16.21. Effect of co-firing on NO_x emissions based on a fixed fuel flow rate.

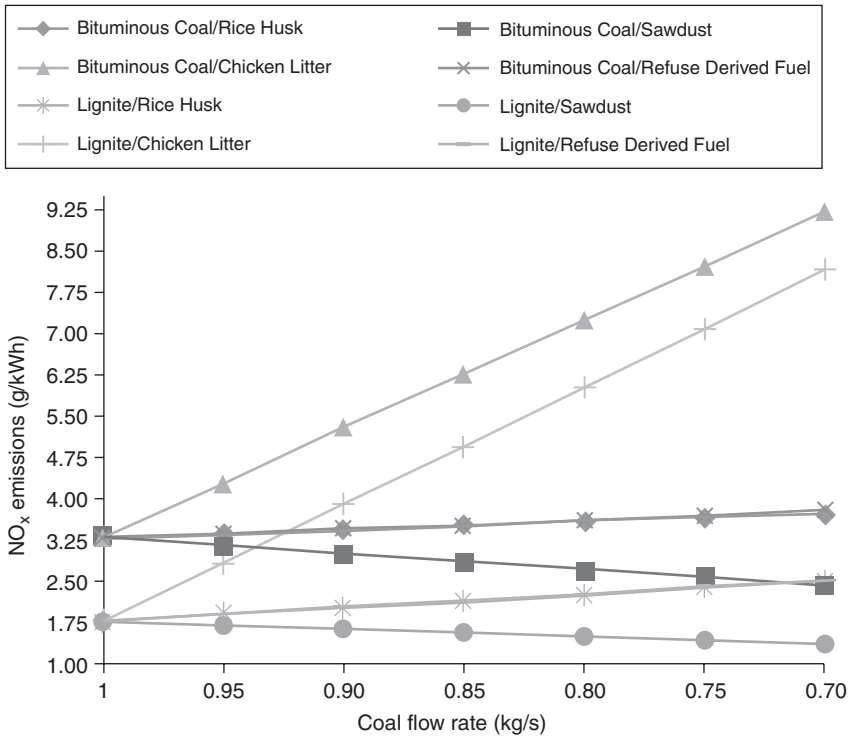


Figure 16.22. Effect of co-firing on NO_x emissions based on a fixed heat input to the steam cycle.

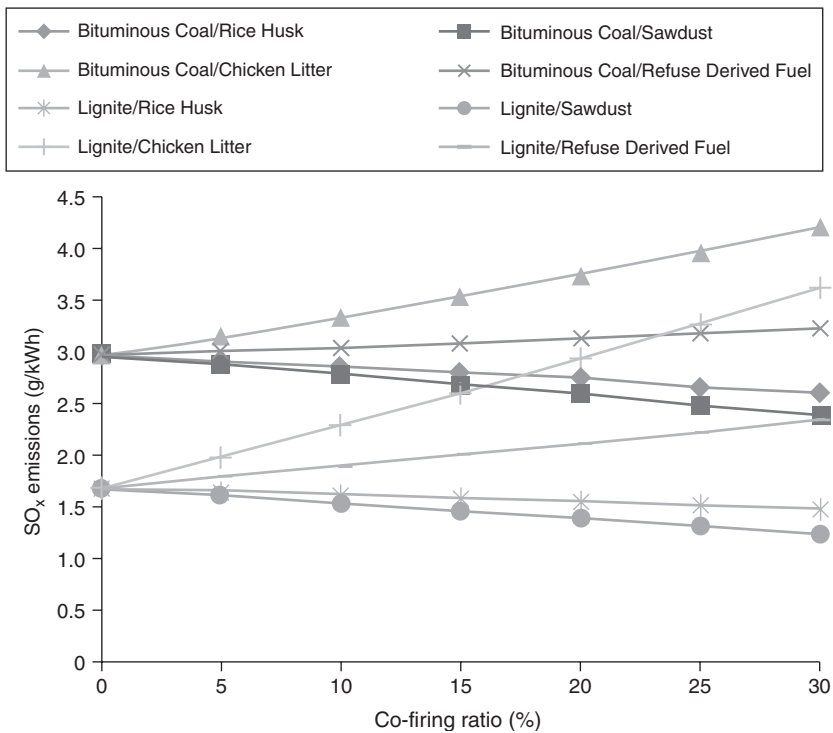


Figure 16.23. Effect of co-firing on SO_x emissions based on a fixed fuel flow rate.

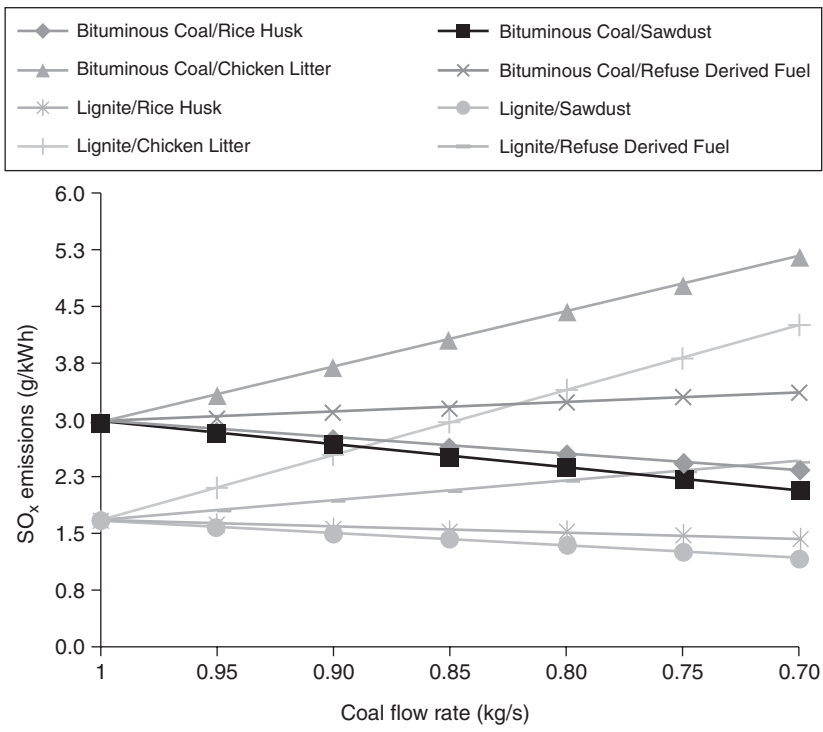


Figure 16.24. Effect of co-firing on SO_x emissions based on a fixed heat input to the steam cycle.

16.7.4.3 Energy-based SO_x emission factors

The effect of co-firing on SO_x emissions is illustrated for cases 1 and 2 in Figures 16.23 and 16.24, respectively. The sulfur content in fuel affects directly the production of sulfur oxides during combustion. Among the chosen biomass types, rice husk and sawdust have negligible sulfur contents, so their addition to a fuel mixture reduces the overall SO_x emissions with co-firing ratio (see Figs 16.23 and 16.24). Since chicken litter has much higher sulfur content than bituminous coal and lignite, the SO_x emission factor increases with co-firing ratio for blends of bituminous coal/chicken litter and lignite/chicken litter. The sulfur concentration of refuse derived fuel is slightly lower than that of bituminous coal. For the case of a fixed fuel flow rate, the SO_x emission factor increases with co-firing ratio for the bituminous coal/refuse derived fuel blend due to a decrease in the work output. However, in the case of a fixed heat input to the steam cycle, the increase in the SO_x emissions with co-firing ratio for the bituminous coal/refuse derived fuel blend is due to an increase in mass of SO_x in the flue gases associated with the large biomass use.

16.8 CONCLUSIONS

The co-firing of biomass with coal has been described thermodynamically, and many important findings highlighted. Energy and exergy efficiencies of both the boiler and the overall plant decrease with increased biomass co-firing. For all biomass fuels considered, the reduction in energy and exergy efficiencies is relatively small at low co-firing ratios (5–10% on a mass basis). However, co-firing results in significantly reduced CO_2 emissions if biomass is considered to be CO_2 neutral. The gross (total) CO_2 emissions are lower if the carbon content of the biomass is relatively low; this characteristic also diminishes the work output reduction caused by biomass

addition to a fuel blend. Moreover, reductions in NO_x and SO_x emissions are also achieved with biomass co-firing with coal if the selected biomass has less nitrogen and sulfur content than coal. Therefore, although co-firing of biomass does not appear to be worthwhile from a thermodynamic perspective because of the reductions observed in energy and exergy efficiencies, co-firing can lead to have substantial benefits in terms of CO_2 , NO_x , and SO_x emissions. Hence, co-firing of biomass with coal has significant environmental benefits and fosters an increased use of renewable energy.

The trends described here can provide plant owners with insights into how a co-firing based system will perform at different co-firing conditions and for different combinations of fuels. Such information is useful for new designs and when retrofitting existing coal-based plants for biomass co-firing. The material covered here enhances the available energy- and exergy-based information regarding biomass co-firing with coal, which to date has been quite limited.

ACKNOWLEDGMENTS

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support.

NOMENCLATURE

C_p	Specific heat at constant pressure [kJ/kg · K]
$\dot{E}$	Energy rate [MW]
$\dot{E}_x$	Exergy rate [MW]
ex	Specific chemical exergy [kJ/kmol]
h	Specific enthalpy [kJ/kg]
$\bar{h}$	Molar specific enthalpy [kJ/kmol]
h^o	Enthalpy of formation [kJ/kmol]
HHV	Higher heating value [kJ/kg]
LHV	Lower heating value [kJ/kg]
$\dot{m}$	Mass flow rate [kg/s]
$\dot{n}$	Molar flow rate [kmol/s]
P	Co-firing ratio [–]
p	Pressure [kPa]
$\dot{Q}$	Heat interaction rate [kW]
T	Temperature [K]
$\dot{W}$	Net work rate produced by system [kW]
s	Specific entropy [kJ/kg/K]

Greek letters

β	Ratio of chemical exergy to lower heating value [–]
η	Energy efficiency [%]
ψ	Exergy efficiency [%]

Subscripts

b	Biomass
C	Carbon
c	Coal
H	Hydrogen
i	Constituent i of a mixture

<i>j</i>	Co-reactant <i>j</i>
<i>in</i>	Inlet
N	Nitrogen
O	Oxygen
<i>o</i>	Reference environment state
<i>p</i>	Products
<i>r</i>	Reactants
<i>out</i>	Outlet
S	Sulfur

Superscripts

<i>Ch</i>	Chemical
<i>o</i>	Standard environment state
<i>Ph</i>	Physical

Acronyms

<i>ar</i>	As received
<i>B</i>	Bituminous coal
<i>BFP</i>	Boiler feed pump
<i>C</i>	Carbon
<i>CL</i>	Chicken litter
<i>CP</i>	Condensate pump
<i>daf</i>	Dry ash free
<i>FWH</i>	Feedwater heater
<i>H</i>	Hydrogen
<i>LPT</i>	Low pressure turbine
<i>HPT</i>	High pressure turbine
<i>M</i>	Moisture
N	Nitrogen
O	Oxygen
<i>RFD</i>	Refuse derived fuel
<i>RH</i>	Rice husk
<i>SD</i>	Sawdust
S	Sulfur
<i>VM</i>	Volatile matter

16.9 QUESTIONS FOR DISCUSSION

- What economic arguments can you see for co-combustion?
- What climatic effect results from co-combustion of coal and biomass?
- What economic incentives would be needed to promote co-combustion?
- How do you value co-combustion in relation to plants using only biomass?
- Why is co-combustion possible in coal-fired plants when it normally is not possible to use pure biomass?

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CHAPTER 17

Control of bioconversion processes

K.P. Madhavan & Sharad Bhartiya

17.1 INTRODUCTION

Modern process plants operate in an environment marked by intense competition on a global scale and a sharper focus on customer satisfaction, safety and environmental compliance along with an increasingly demanding and dynamic market place. Keeping these imperatives in view, current and emerging plants of the future may need to be designed with an emphasis on energy conservation and optimal use of all resources. This would result in integrated plant configurations, which have tightly coupled process units with internal recycling, reduced inventories and regulated waste discharge. The competitive environment in which a modern plant operates, calls for operation at maximum levels of productivity while maintaining product quality within specifications and operating within equipment and operational safety constraints.

Typically, the process plant is designed for some nominal conditions for feedstock quality and environmental variables. However, variations in these variables during the operation of the plant, termed as disturbances, are almost certain and need to be handled efficiently. These disturbances can be classified into (i) plant-related, and (ii) economic-related. The plant-related disturbances may be further classified as follows:

- *Supply side disturbances*: variation in the raw material quality and availability.
- *Demand side disturbances*: fluctuations in product demand and quality (grade).
- *Utility side disturbances*: uncertainties in supply and quality of utilities like electrical power, steam, fuel, air, water (cooling tower circulation, chilled or brine) and refrigeration.
- *Equipment performance degradation*: significant deviation of equipment performance from its design values such as during fouling in heat transfer equipment, loss in catalytic activity and channeling in packed beds.

Since profitability, in addition to safety, is the ultimate goal of plant operation, fluctuations in sale value of products, cost of raw materials and utilities represent the economic-related disturbances, which influence the manner in which the plant needs to be operated. Moreover, all operating and control strategies need to ensure that the plant operates within prescribed constraints on holdup, operating variables (temperature, pressure) and performance related constraints (flooding, surge).

The complexities in the configuration and operation of modern plants pose many challenges for process control. As an example, consider the wood pulp manufacturing plant based on the Kraft process, whose process flow diagram is shown in Figure 17.1 (Castro and Doyle, 2004a,b). The Kraft pulping plant has four major sections – pulp digestion, bleaching, chemical recovery and paper making:

- *Pulping*: In the digester, wood chips are treated with white liquor (solution of NaOH and NaSH) at conditions of temperature, which promote efficient delignification of wood chips. Key quality variables are the Kappa number of the pulp at discrete points in the digester, representing the progressive degree of cooking. Other variables that may be used to monitor the pulp quality include the concentration of active alkali of the entering white liquor as well as in the spent liquor exiting from the digester.

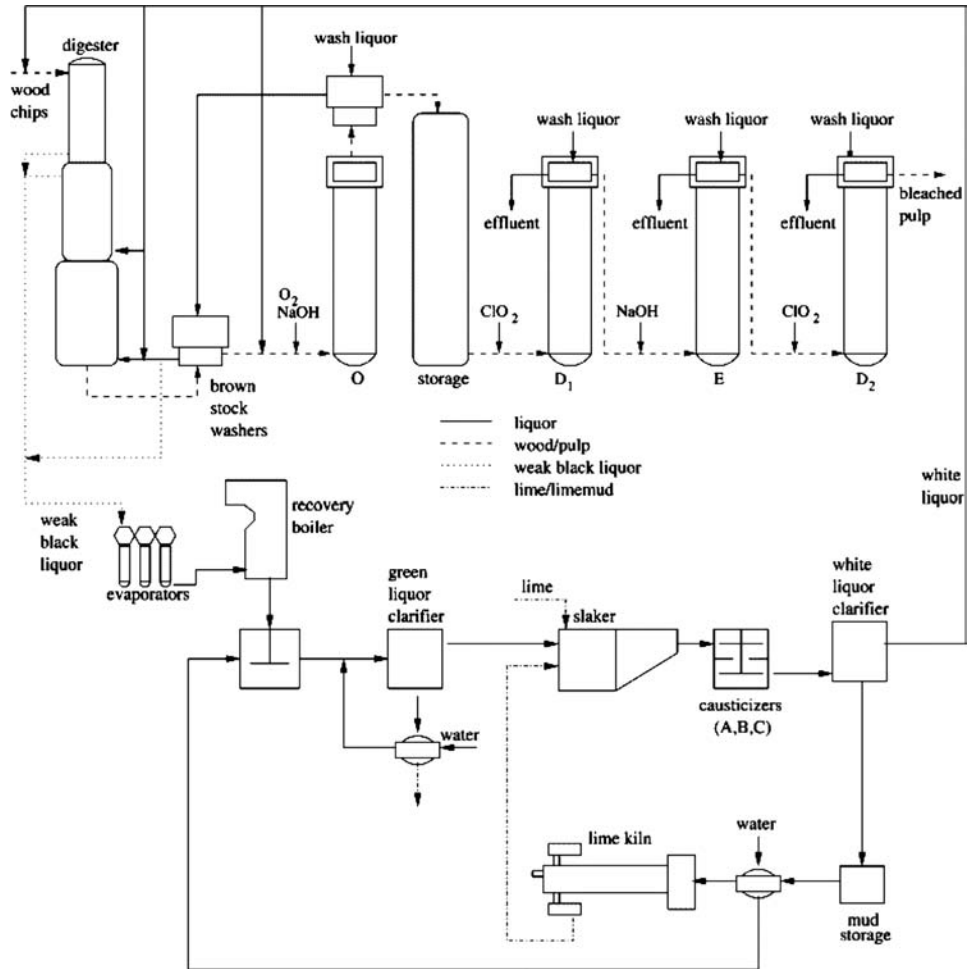


Figure 17.1. Process flow diagram of a modern pulping mill based on Kraft process (taken with permission from Castro and Doyle, 2004a).

- Bleaching:** The pulp from the digester is then sent to the bleach plant, which consists of a series of reactions, each occurring in separate columns. The first column (O) uses oxygen and alkali $NaOH$, the second (D_1) and fourth (D_2) columns use ClO_2 , and the third column (E) uses $NaOH$. The key variables in the bleaching section, which indicate quality, are the Kappa number of exit pulp and brightness of pulp from the D_2 tower.
- Chemical recovery:** The chemical recovery section consists of multiple effect evaporators, which concentrate the weak black liquor to a concentration level of 60–65%. The concentrated black liquor is used in the recovery boiler to generate steam. The residue melt is treated in a sequence of units like green liquor clarifier, slaker, where $NaOH$ and $NaSH$ are recovered. The mud from the clarifier is sent to a lime kiln to recover $Ca(OH)_2$. Besides the temperatures and levels in each of the evaporators, lime residual carbonate and active alkali of first causticizer are key quality variables. Appropriate controls need to be exercised to maintain desired concentration levels of $NaOH$ and $NaSH$. There are recycle streams in each of the sections and recycle streams across various sections. These recycle flows need to be controlled to

ensure stable operation. Absence of chemical recovery makes the Kraft process economically unviable.

- *Paper-making*: The paper making section consists of machine chest, stuff box, head box, moving paper forming screen and underflow recycle from the screen to the stuff box (not shown in Fig. 17.1). The wet paper sheet coming out of the paper-forming section goes to the dryer section. Key variables of the paper machine are the cross-direction and machine direction of basis weight and moisture content.

Castro and Doyle (2004a,b) have identified a total of 114 outputs and 142 inputs for the process shown in Figure 17.1. If the paper machine is also included then the variable count becomes significantly larger. Disturbances exist in the quality of wood chips, temperatures and concentrations of incoming chemical streams. Because of recycle streams, these disturbances propagate downstream as well as upstream causing deviations in the desired variables for extended periods of time.

Besides these control requirements stated above, pulp and paper mills make different grades of pulp and paper. These grades depend on customer orders, as well as the prevailing market conditions. This calls for implementation of strategies that decide the optimal sequence of grades to be made which minimize the amount of off-specification product made during the grade transition. Further, the sequence must ensure that various customer order and delivery constraints are satisfied. These considerations form part of the production scheduling. Thus, it can be seen that plant operation is a large dimensional problem. From the plant-wide control point of view, the tasks of disturbance rejection, safety enforcement and profit optimization are realized through a spatial, functional and temporal decomposition of various control tasks. The control structure, which has emerged over decades of process control practice, is hierarchical with different levels as shown in Figure 17.2. The various tiers of the control structure can be described as follows:

- *LEVEL 0 – Local control*: Control of single variables like Kappa number, brightness, temperature, effective alkali, pressure, density, levels at appropriate points in the process structure.
- *LEVEL 1: Advanced control*: Regulatory and tracking control of process units like digester, bleach plant, units in the chemical recovery section, paper machine and dryer, while ensuring that process specification and safety constraints are satisfied.
- *LEVEL 2: Process unit optimization*: This layer looks at profitable operation of each process unit and calculates economically optimal set points, which are enforced through Level 1. It can also specify the control sequences for grade change.
- *LEVEL 3: Plant wide control and optimization*: This uses a plant level model to determine the plant optimum and co-ordinate the operation of unit level optimizers so that collectively they drive the plant optimum closer to the optimal targets.
- *LEVEL 4: Production scheduling*: The scheduler receives production targets for various grades of product from the planning layer along with delivery schedules. The scheduler has to suitably allocate production schedule for manufacturing of various grades so as to utilize optimally the production capacity at minimal cost.
- *LEVEL 5: Production planning*: This layer decides the portfolio of product grades to be made based on the demand pattern, production capacity and profitability.

The decomposition is primarily possible due to different time-horizons at each level. For example, the local controllers at Level 0 operate in the range of milliseconds whereas the plant unit optimization at Level 2 may operate once a shift. Similarly, scheduling and planning activities have typical horizons of weeks and months, respectively. As evident from Figure 17.2, the different control strategies use different types of models to quantify the process behavior. Understanding the static and dynamic behavior of processes to be controlled is critical for realization of effective control for the same.

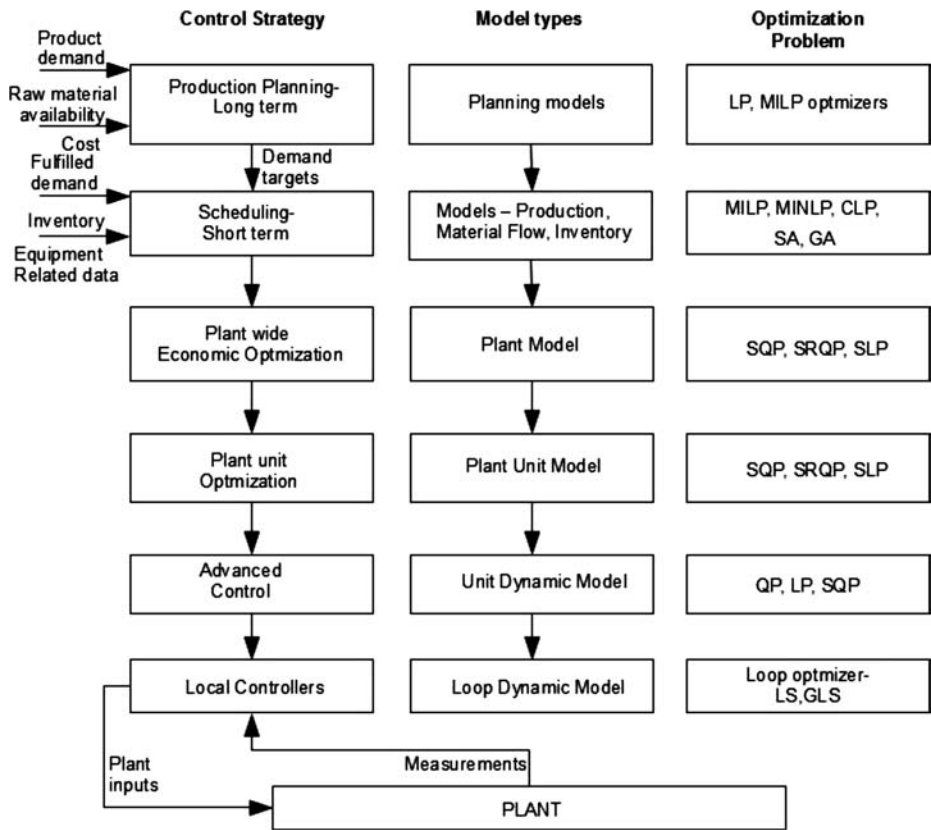


Figure 17.2. Hierarchical decomposition of control strategies based on time-scales. Also shown are model types and the optimization problems that are encountered.

17.2 PROCESS DYNAMICS

The ease of controlling a process depends on its static and dynamic behavior. Control system design must ensure corrective actions at rates compatible with the dynamic response of the process and its accessory equipment. Thus, process dynamics play an important role in deciding the structure of an appropriate process control system. The dynamics of a process control loop are affected by various elements in the loop such as process, measurement system, controller, actuator, etc. While a process engineer is usually conversant with the dynamic behavior, it is the process model that provides a quantitative description and can be gainfully used for process control. These models vary from physico-chemical models, which use first-principles to black-box models, which are purely data-driven.

17.2.1 Physico-chemical models

Bioconversion processes are operated in three modes namely, batch, fedbatch and continuous. Many bioconversion processes such as saccharification, fermentation and neutralization are characterized by strong nonlinear behavior. For example, in fedbatch fermentation processes, models for growth and product formation show long dead- times during induction, followed by an exponential increase in biomass and a saturating behavior during the stationary phase. Similarly, strong acid-strong base neutralization depicts a strong nonlinear behavior. These various behaviors can

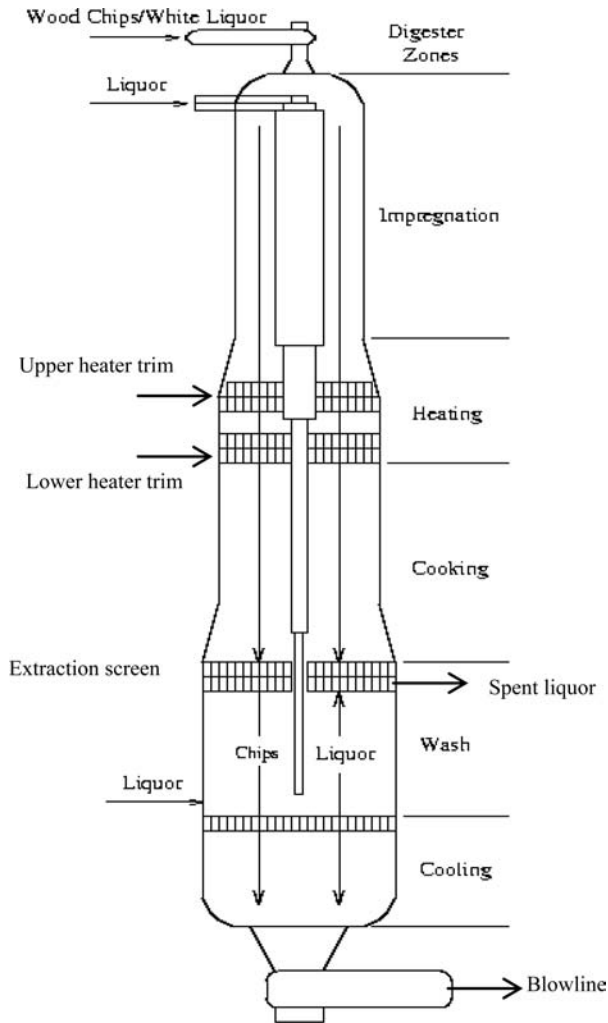


Figure 17.3. Schematic of a single vessel continuous digester (with permission from Bhartiya *et al.*, 2003).

be captured with the aid of a process model. In this chapter, we use the Kraft pulping process in a single vessel continuous digester as the main example around which the various control strategies are illustrated.

17.2.1.1 Single vessel continuous digester for wood pulping

Pulping mills convert wood chips to pulp suitable for paper production by displacing lignin from digesters where the chips react with an aqueous solution of sodium hydroxide and sodium sulfide, known as white liquor, at elevated temperature. Most continuous digesters consist of three basic zones: an impregnation zone, a cooking zone and a wash zone. A schematic of a single vessel digester is shown in Figure 17.3 (Bhartiya *et al.*, 2003). White liquor and pre-steamed chips are introduced at the top of the digester into the impregnation zone where the liquor penetrates the wet chips. However, the majority of the delignification reaction occurs only after the two streams flow downward into the subsequent cooking zone where the mixture is heated to reaction temperatures achieved by liquor circulation through external heaters. The spent liquor is withdrawn from the

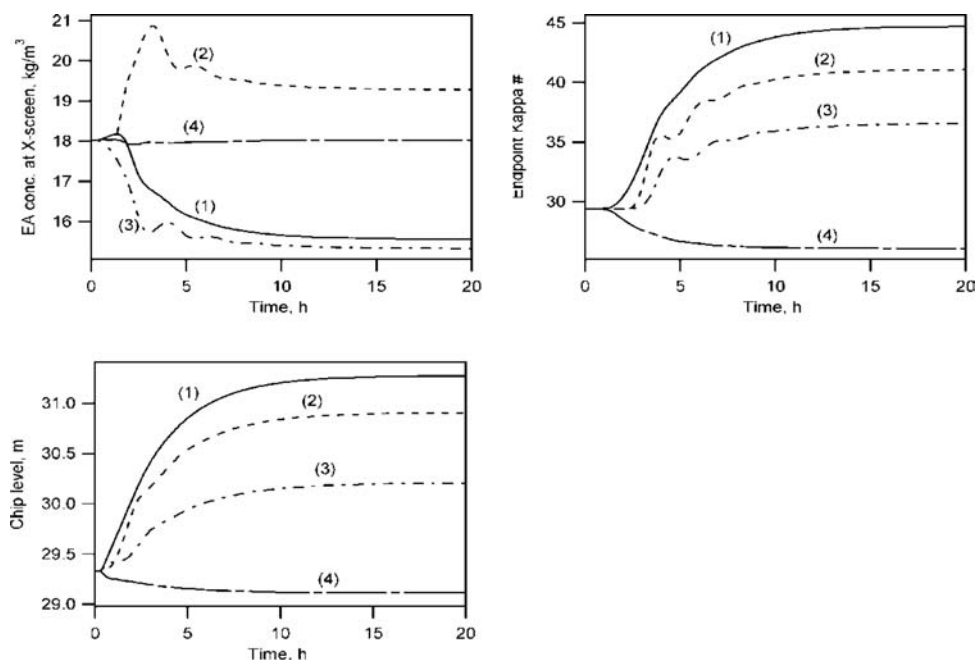


Figure 17.4. Dynamic behavior for (1) increase in blowline flow; (2) decrease in upper heater temp.; (3) decrease in white liquor; and (4) decrease in dilute liquor flow (taken with permission from Bhartiya *et al.*, 2003).

digester at extraction screens located at the end of the cook zone while the cooked chips continue the downward journey to the wash zone. Here, the chips are washed by the countercurrent flow of cold, dilute liquor. This effectively quenches the delignification reaction. The quality of the resulting pulp is described by Kappa number, which is a measure of the residual lignin content. A typical control objective of digester operation is to minimize variation in the Kappa number from a prescribed value.

17.2.1.2 A physico-chemical model for the pulp digester

From a modeling perspective, the interplay between heat, mass and momentum transport during the thermal-hydraulic degradation of the wood chips makes the system coupled. For example, softening of the chips, as cooking proceeds, causes them to compact more densely, which in turn affects the chip movement. On the other hand, large transport delays, complex dynamics, biological feedstock variability, and process integration make control applications difficult. The temporal variations of the various wood and liquor components are described by conservation of mass, energy and momentum, resulting in a set of coupled nonlinear PDEs, which may be solved by numerical methods such as finite differences or orthogonal collocation on finite elements. For the sake of brevity, we do not repeat these equations here but cite Bhartiya *et al.* (2003) as a ready reference and the results characterizing the dynamic behavior are briefly reviewed below.

Dynamic behavior of the digester is characterized by large dead times in primary measurements, such as the endpoint Kappa number. Figure 17.4 shows model predictions for effective alkali (EA), a measure of the strength of the active alkali, at the extraction screens, the blowline Kappa number and the chip level in the digester for step changes in various inputs. These input changes include filtered step changes in (1) blowline flow, (2) cooking circulation upper heater temperature, (3) white liquor and (4) dilute liquor flows of $0.15 \text{ m}^3/\text{min}$, -10°C , $-0.15 \text{ m}^3/\text{min}$ and $-0.15 \text{ m}^3/\text{min}$, respectively. In each of the cases, the relation between the endpoint Kappa number and chip level

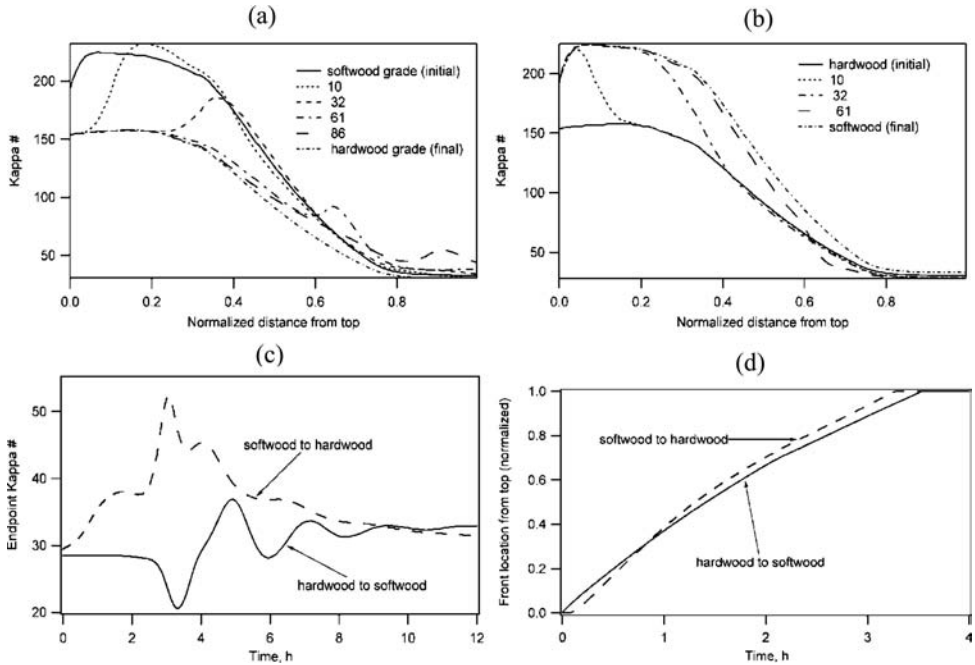


Figure 17.5. (a), (b) Kappa profile snapshots when the softwood (hardwood) to hardwood (softwood) transition front is at different locations. The numbers in the legend refer to the control volume in which the front lies when the snapshot is taken. Appropriate changes were made to the heater temperatures to achieve acceptable endpoint Kappa numbers. (c) Endpoint (blowline) Kappa number transients for grade change transitions. (d) Dynamic trajectory of transition front for the two cases of grade transition. Grade transition is modeled by assuming a discrete transition front (Taken with permission from Bhartiya *et al.*, 2003).

is apparent, as they are coupled *via* residence time. Cases 1 and 3 result in lower cooking due to lower rate of availability of chemicals, while lower cooking in case 2 is due to smaller amounts of available energy. The decrease in the chip level in case 4 is due to the lower “lift” provided by the reduced dilute liquor flowrate. In each of the four cases, changes in levels are due to rearrangement of the chip compaction profile. Thus, the dynamic model provides information about the sensitivity of the various variables such as endpoint Kappa number to the inputs as well as the nature of the transient behavior.

Pulping mills often switch the feedstock grade from hardwood to softwood and vice versa to satisfy demands from the downstream paper machine section. Such grade changes inevitably have large transition times associated with them. Figure 17.5a shows model predictions for the Kappa number profile snapshots at different times during a feed transition from softwood to hardwood. The grade swing was obtained with an open loop operating policy that involved decreasing the upper and lower heater temperatures from 429 to 416 K and 443 to 424 K, respectively, when the front location, reached the respective heater locations. In addition, the white liquor flow rate to top of the digester was decreased by 40% after the transition front crossed the extraction screens. Figure 17.5d shows the dynamic trajectory of the front location as the hardwood species completely fills the digester. It is noted that after two hours of grade change implementation, the grade transition front traverses about 68% of the digester length (Fig. 17.5d) and the chips beyond the front location (softwood) are severely undercooked as evident from the high endpoint Kappa number (dashed line in Fig. 17.5c). The insufficient cooking takes place despite of the 30-minute delay in increasing the heater temperatures as discussed above. This is expected since the

softwood, which has not completely exited from the digester, is subjected to the milder cooking appropriate for hardwood (less temperature, less chemicals). Thus, in a softwood to hardwood transition, the reduction in the energy and cooking chemicals, in anticipation of the reduced lignin content of the new grade, results in lower cooking (or higher Kappa number) during the transition time. The opposite case of transition of the feedstock grade from hardwood to softwood is presented in Figure 17.5b. After two hours of operation, the grade transition front traverses approximately 63% of the digester length where severe overcooking is noted (solid line in Fig. 17.5c). The under-shoot in the hardwood to softwood transition represents the overcooking of the older hardwood grade. Aggressive operating condition changes in anticipation of the grade change can potentially plug the digester. This observation is consistent with the mill experience that a hardwood to softwood transition is more “problematic” than *vice-versa*. An interesting industrial case study on digester plugging is discussed in Bhartiya and Doyle (2004). Both the transitions are similar, with softwood to hardwood transition occurring more quickly than the hardwood to softwood transition.

Development of a first principles model such as that of the digester discussed above represents a time-consuming and expensive task of quantifying the process dynamics. It includes estimating various parameters (for example the heat transfer coefficient, heat of reaction, etc.), which are then used with conservation laws to obtain the dynamic picture. While such models are able to capture the qualitative behavior for a diverse set of operating conditions and provide operating insights, the representation may not be quantitatively accurate. Moreover, the model is computationally complex for effective use in online applications such as in advanced control. In such cases, it may be beneficial that simpler, approximate linear models are developed that describe the relationships between inputs (such as manipulated variables) and outputs (such as measurements of quantities of interest) of the system. A significant advantage of these models is that they can be rapidly identified from the process data directly. These models, however, are usually accurate only in a small vicinity of the operating point around which they are developed. In the next section, we discuss a few representative approximate models that can mimic the dynamic behavior of many industrial processes.

17.3 APPROXIMATE MODELS TO CAPTURE ESSENTIAL DYNAMICS

In this section, we explore simple dynamic behavior, which forms the basis for the design of many controllers and control systems designed for certain steady state performance of process equipment. These processes have, by necessity, elements, which store mass or energy (capacitance element), and resistive components which resist the flow of mass or energy. Such resistance-capacitance networks cause a lag (time constant) in the dynamic response of system to a change at its input. The dynamic behavior of the system depends on the number of such capacitance elements and the nature of interconnection between the capacitive components.

17.3.1 Single capacity element: first order system

A first order system can be represented by a tank of area A , which can store mass (capacitance) and a valve (resistance R) which can regulate the outflow (Fig. 17.6). Assume that the level of liquid whose density is ρ is at a steady value of h_s , when the inflow is held at $q_{in,s}$. Any deviation in the inflow Δq_{in} from $q_{in,s}$ will result in a transient behavior in the deviation of level Δh from h_s and is related to Δq_{in} as follows:

$$A\rho\frac{d\Delta h}{dt} = \rho\Delta q_{in} - \rho\Delta q_{out} = \rho\Delta q_{in} - \rho\frac{\Delta h}{R} \quad (17.1)$$

Note that the outflow has been deliberately modeled as linearly varying in height. A linear dynamic model enables use of a variety of tools for synthesis of controllers and analysis of the closed loop dynamic system. For ease in analysis and design of control systems, the model in

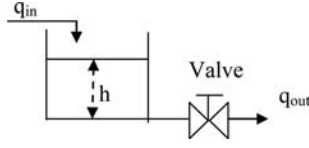


Figure 17.6. First order system: single tank followed by a linear valve.

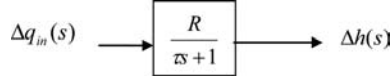


Figure 17.7. Block diagram representation of first order system.

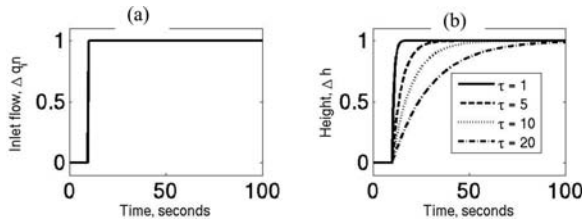


Figure 17.8. Typical response of a first order system for a step change in input.

time domain is translated into the Laplace or s domain through a linear transformation known as Laplace transformation defined as follows:

$$L[\Delta h(t)] = \int_0^{\infty} e^{-st} \Delta h(t) dt = \Delta h(s) \quad (17.2)$$

Applying the Laplace transform to both sides of equation (17.1), we get:

$$AL \left[\frac{d\Delta h}{dt} \right] = A[s\Delta h(s) - \Delta h(0)] = \Delta q_{in}(s) - \frac{\Delta h(s)}{R} \quad (17.3)$$

where $\Delta h(0) = h(0) - h_s$ and the initial level is assumed to be at the steady state level, that is, $\Delta h(0) = 0$. Thus, one can write the dynamic relationship between the output Δh and input Δq_{in} in a transfer function form as follows:

$$\frac{\Delta h(s)}{\Delta q_{in}(s)} = \frac{R}{\tau s + 1} = \text{Transfer function} \quad (17.4)$$

where $\tau = AR$ represents the time constant of the process and R the process gain, that is, the change in output for a unit change in input. The relationship between the process input and output can be described by the block diagram shown in Figure 17.7.

The time constant is an indicator of the speed of response of a first order system. Figure 17.8b shows the response of the first order process for various time constant values for a unit step change in the input variable (Fig. 17.8a). It can be seen from the responses that a larger time constant indicates a sluggish response. This is because larger time constants imply larger holdup volume and hence a slower response.

In the above formulation, $h(t)$ is also called as the state variable as it represents the holdup of material and hence the state of the system. Similarly, in a first-order thermal system of constant

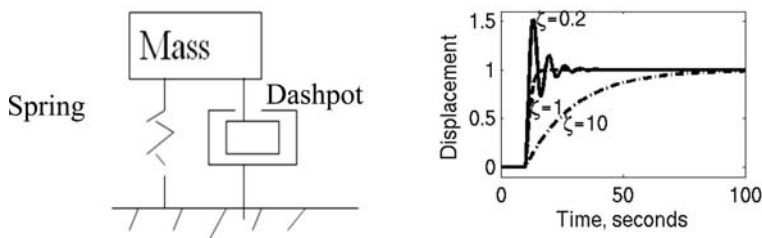


Figure 17.9. (a) Second order system representation using mass-spring-dashpot components; (b) Typical response of a second order system to a unit step change in input.

mass and specific heat, the temperature represents the energy stored in the element and hence qualifies as a state variable. In a closed volume under isothermal conditions, pressure indicates the amount of mass stored and hence a state variable. Measurements of state variables are referred to as outputs.

17.3.2 Second order system

In an inherently second order system like mass, spring and damper, there are two elements that store energy namely, mass and spring. Energy dissipation is due to damper or (dashpot) (Fig. 17.9a). Models of second order systems can be described by the inertial force being equilibrated by a spring and a dashpot. Thus, the governing equation is:

$$M \frac{d^2x}{dt^2} = f - Kx - B \frac{dx}{dt} \quad (17.5)$$

where M represents the mass, x , displacement, f the applied force; K and B represent the spring constant and the damping coefficient, respectively. The following terms are normally defined:

$$\zeta = \text{damping ratio} = \frac{B}{2\sqrt{KM}}, \quad \omega_n = \text{undamped natural frequency} = \sqrt{\frac{K}{M}}$$

Through appropriate manipulation of terms this can be cast into the transfer function form:

$$\frac{\Delta x(s)}{\Delta f(s)} = \frac{\omega_n^2 / K}{s^2 + 2\zeta\omega_n s + \omega_n^2} \quad (17.6)$$

Typical second order responses for a step change in the input are shown in Figure 17.9b. A second order system can be characterized as overdamped (damping ratio > 1), critically damped (damping ratio $= 1$), and underdamped (damping ratio < 1). As the damping ratio becomes less than unity, the response to a step change shows under damped oscillation. Note that a second order system can also be obtained by a combination of two first order system in series. However, its step response will be aperiodic with no oscillation. On the other hand, an inherently second order of system can show oscillatory response.

17.3.3 Dynamics of higher order processes

The presence of a number of holdups in process equipment leads to a higher order process or what is termed as multi-capacity process. A hypothetical n th order system is a cascade of n tanks in series (Fig. 17.10a). An inflow stream with solute concentration C_{in} goes through the n well mixed tanks. In this system, there are n state variables, $C_1, \dots, C_n$. Since the outlet concentration is the one of interest, the output variable is C_n .

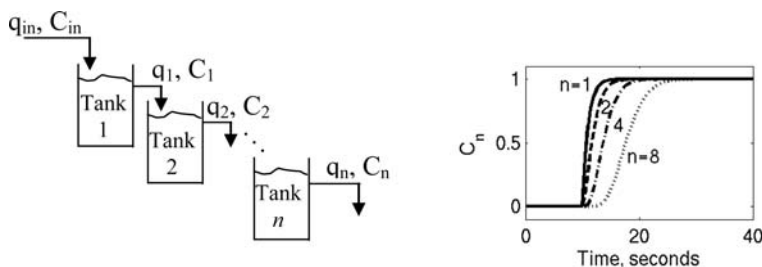


Figure 17.10. (a) An n th order system can be represented as n tanks in series; (b) typical response of n th order system. As the order increases, the response becomes sluggish.

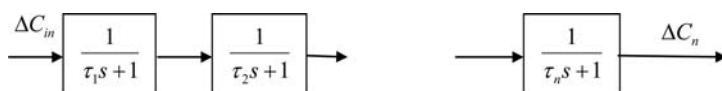


Figure 17.11. Block diagram representation of an n th order system as n first order systems in series.

A step change in inlet concentration will cause concentration responses as shown in Figure 17.10b. Note that the concentration response becomes slower as the number of tanks and hence the model order increases.

The dynamic model for the i th stage is given by:

$$V_j \frac{dC_j}{dt} = qC_{j-1} - qC_j \quad (17.7)$$

The transfer function for j th stage is given by:

$$\frac{\Delta C_j(s)}{\Delta C_{j-1}(s)} = \frac{1}{\tau_j s + 1} \quad \text{where } \tau_j = \frac{V_j}{q} \quad (17.8)$$

By combining the transfer functions for the n stages one can get the overall transfer function relating the feed concentration ΔC_{in} to the output concentration ΔC_n :

$$\frac{\Delta C_n(s)}{\Delta C_{in}(s)} = \prod_{j=1}^n \frac{1}{\tau_j s + 1} \quad (17.9)$$

The block diagram of the system is shown in Figure 17.11. In such a process equipment, the holdups for mass and energy can become very large, of the order of three or more. A distillation column with N stages will have at least $3N$ capacitances.

17.3.4 Pure time delay processes

Time delay, often called transport delay, is characterized by the time taken by a fluid element to traverse across a pipe of length D with a finite velocity V . Thus, as shown in Figure 17.12a, the inlet concentration of the feed is delivered at the output after the transport lag $L = D/V$ time units. The transfer function of the pure time delay process is given as:

$$\frac{\Delta C_n(s)}{\Delta C_{in}(s)} = e^{-Ls} \quad (17.10)$$

Such transport delays are ubiquitous in the process industry. A common modeling approach involves representing the lag caused by high order process as a pure time-delay (see section 17.3.5).

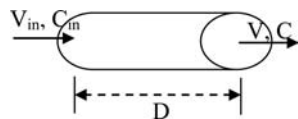


Figure 17.12. A pure time delay representation as a plug flow in a pipe; the output of the pure time delay process is simply the input delayed by time needed to traverse the pipe length.

Table 17.1. Summary of approximate models.

Model Order	Model equation	Transfer function	Step response characteristics
First Order: one tank system (Figs. 17.6–17.8)	$A \frac{dx}{dt} = q_i - \frac{h}{R}$	$\frac{R}{\tau s + 1}$	As τ increases, settling time increases
Second Order: Mass-spring-dashpot (Fig. 17.9)	$M \frac{d^2 \Delta x}{dt^2} = -B \frac{d\Delta x}{dt} - K\Delta x + f$ $M = \text{mass}; B = \text{damping factor}; K = \text{spring coefficient}; f = \text{force}; \Delta x = \text{position}$	$\frac{\Delta x(s)}{\Delta f(s)} = \frac{\omega_n^2 / K}{s^2 + 2\zeta\omega_n s + \omega_n^2} \frac{B}{B}$ $\zeta = \text{damping ratio} = \frac{B}{2\sqrt{KM}}$ $\omega_n = \text{natural frequency} = \sqrt{\frac{K}{M}}$	$\zeta > 1$: over damped $\zeta = 1$: critically damped $0 < \zeta < 1$: under damped ω_n : frequency of oscillation when $\zeta = 0$
Higher Order (multicapacity): Mixing tanks (first order systems) in series (Figs. 17.10, 17.11)	$\tau_1 \frac{d\Delta C_1}{dt} = \Delta C_{in} - \Delta C_1$ $\tau_2 \frac{d\Delta C_2}{dt} = \Delta C_1 - \Delta C_2$ $\vdots$ $\tau_n \frac{d\Delta C_n}{dt} = \Delta C_{n-1} - \Delta C_n$ $\tau_i = \text{time constant of } i\text{th mixing tank}$ $\Delta C_i = \text{concentration of } i\text{th mixing tank}$	$\frac{\Delta C_n(s)}{\Delta C_{in}(s)} = \prod_{i=1}^n \frac{1}{(\tau_i s + 1)^n}$	As n increases, step response gets slower. At higher values of n , the response shows a delay similar to pure time delay or transportation lag
Pure Time Delay or Transportation Lag: Plug flow in a pipe (Fig. 17.12)	$\Delta C(t) = \Delta C_{in}(t - L)$ $L = \frac{D}{V} = \frac{\text{Length of pipe}}{\text{Velocity of liquid}}$ $\Delta C_{in} = \text{inlet concentration}$ $\Delta C = \text{output concentration}$	$\frac{\Delta C(s)}{\Delta C_{in}(s)} = \exp(-Ls)$	Pure time delay or transportation lag causes a delay before reacting to input changes

In the case of the pulp digester, these delays may be apparent delays due to the presence of multiple or distributed capacitances in the dynamic path between the process input and output or true time delay in the manipulated variable reaching the reaction phase, delay in sensing the output.

As the number of capacitances n or order of the high-order system increases or if the ratio of the time delay L to the dominant time constant in the process becomes large, it becomes difficult to control the system. This is typical of dynamics of digesters, which has distributed capacitances (or infinite capacitances) across its length, which causes a large time delay in its response with response time in hours. Table 17.1 summarizes characteristics of these systems.

17.3.5 Control relevant models for process control systems design

Dynamic models of large reactors and digesters can be modeled as multi-capacity systems and thus with models of very high order. However, if the processes do not exhibit strong nonlinearity, lower order linear transfer models are often sufficient for design of a control system. These usually have the form of simpler dynamic models involving time constants and time delay. Two such model forms are given below:

Model 1: First Order Plus Time Delay (FOPTD)

$$\frac{K_p e^{-Ls}}{\tau s + 1} \quad (17.11)$$

Model 2: Second Order Plus Time Delay (SOPTD)

$$\frac{K_p e^{-Ls}}{(\tau_1 s + 1)(\tau_2 s + 1)} \quad (17.12)$$

There could be further modifications to these two basic forms of the model by introduction of an integrator ($1/s$) or a numerator term (zero) of the form $(\xi s + 1)$.

Model 3: First Order Plus Time Delay Plus An Integrator

$$\frac{K_p e^{-Ls}}{s(\tau s + 1)} \quad (17.13)$$

Model 4: First Order Plus Time Delay Plus A Single Zero

$$\frac{K_p(\xi s + 1)e^{-Ls}}{(\tau_1 s + 1)} \quad (17.14)$$

Model 5: Second Order Plus Time Delay Plus A Single Zero

$$\frac{K_p(\xi s + 1)e^{-Ls}}{(\tau_1 s + 1)(\tau_2 s + 1)} \quad (17.15)$$

Note that roots of the denominator are termed as poles while roots of the numerator are called zeros. An advantage of such models is that they can often be obtained directly from the response data generated through plant tests, which consist of perturbing the inputs to the plant. In the remainder of this section, we describe the dynamic behavior of the digester using the 5 simple linear models discussed above. The first-principles model discussed in section 17.2 is used as a proxy for the real plant.

17.3.6 Linear system identification: single-vessel digester case study

We assume that the single vessel digester has online Kappa measurements available at four different locations along the digester (see Fig. 17.3) namely, upper and lower heaters, extraction screens, and blowline, as indicators of the Kappa profile. Although, online Kappa measurements are generally infrequent (once in 20 minutes), schemes for inferring Kappa numbers using readily available measurements have been reported in literature (Paulonis and Krishnagopalan, 1988; Wisniewski and Doyle, 1998; Amirthalingam and Lee, 2000) and can be employed to obtain estimates. A summary of the control problem is provided below:

- *Controlled variables:* Kappa number at upper heater, Kappa number at lower heater, Kappa number at extraction screens, Kappa number at blowline (end-point) and the residual effective alkali at the extraction screen (see Fig. 17.3 for details)
- *Manipulated variables:* Upper heater temperature, lower heater temperature, makeup white liquor to upper heater, makeup white liquor to lower heater and white liquor flow at top of digester (see Fig. 17.3 for details)

- *Measured disturbance*: Feedstock grade transition from hardwood to softwood treated as a binary switch (Doyle *et al.*, 2001).
- *Unmeasured disturbance*: Step change in white liquor EA, which affects all three white liquor flow variables in the manipulated input.

Note that the dynamics during planned grade transition from hardwood to softwood is captured by simply setting the measured disturbance flag to unity. In absence of transition the value of the disturbance flag is maintained at zero. Linear transfer function models (first order plus time delay (FOPTD), FOPTD with single zero, second order plus time delay (SOPTD), and SOPTD with single zero) were identified from data generated by step tests. The resulting transfer function matrix (between outputs, manipulated inputs and the measured disturbance) is displayed in Table 17.2. Note that all transfer function models belong to the family of control-relevant models described above. Figure 17.13 shows comparison of residual EA prediction by a SOPTD with a single zero model with the fundamental model when the lower heater temperature is decreased by 5 K. Model validation results for a series of changes in the model inputs are depicted in Figure 17.14.

17.3.7 Discrete-time models for sampled data system

With the advent of modern microprocessor-based controllers, continuous process models have given way to discrete models since these controllers work on data sampled at a fixed sampling frequency (100–5000 ms). Between every two samples, the input is maintained constant at its initial value. A schematic of the sampled data system is shown in Figure 17.15. Thus, the continuous time linear systems can be integrated between two consecutive samples to yield models that can be represented by difference equations. Thus integrating the differential equation for the first order process in equation (17.1) with a sample time of T between the k and the $(k+1)$ st sample, we obtain:

$$h((k+1)T) = \left[\exp\left(-\frac{T}{\tau}\right) \right] h(kT) + q_{in}(kT) \frac{R}{\tau} \int_{kT}^{(k+1)T} \exp\left(-\frac{(k+1)T - \sigma}{\tau}\right) d\sigma \quad (17.16)$$

where it is assumed that:

$$q_{in}(t) = q_{in}(kT); \quad kT \leq t < (k+1)T \quad (17.17)$$

Thus, the discrete time linear model can be written as a difference equation as follows:

$$h((k+1)T) = ah(kT) + bq_{in}(kT); \quad a = \exp\left(-\frac{T}{\tau}\right), \quad b = \frac{R}{\tau} \int_{kT}^{(k+1)T} \exp\left(-\frac{(k+1)T - \sigma}{\tau}\right) d\sigma \quad (17.18)$$

where parameters a and b are model coefficients, which can be readily identified by comparing with equation (17.16). A key advantage in writing the model in the difference form is that the model parameters can be estimated from the plant data directly by linear least squares estimation methods (see for example, Oggunnaik and Ray, 1994).

The discrete-time model is usually expressed after dropping T from the above equation. Thus:

$$h(k+1) = ah(k) + bq_{in}(k), \quad (17.19)$$

The second order discrete-time model has the form:

$$x(k+1) = a_2x(k) + a_1x(k-1) + b_0u(k) + b_1u(k-1) \quad (17.20)$$

Table 17.2. Linear models identified for the digester control problem (time: seconds, flow rates: m³/s, effective alkali: kg/m³ as NaOH).

	Upper heater temperature	Lower heater temperature	Makeup liquor to upper heater	Makeup liquor to lower heater	White liquor flow to top of digester
Upper heater Kappa #	$\frac{-2021s - 0.29}{10040s + 1}e^{-200s}$	0	$\frac{-151.3}{7289s + 1}e^{-7500s}$	0	$\frac{-66.58}{7393s + 1}e^{-14000s}$
Lower heater Kappa #	$\frac{-5791s - 1.25}{8429s + 1}e^{-1100s}$	$\frac{-0.64}{3982s + 1}e^{-7000s}$	$\frac{3.04e05s - 1164}{9308s + 1}e^{-1700s}$	$\frac{-587.3}{8268s + 1}e^{-8400s}$	$\frac{-735.9}{9364s + 1}e^{-3400s}$
Extraction screen Kappa #	$\frac{-1.2}{9013s + 1}e^{-3600s}$	$\frac{-4312s - 2.6}{9015s + 1}e^{-2800s}$	$\frac{-2769}{8881s + 1}e^{-3600s}$	$\frac{-2998}{8919s + 1}e^{-2700s}$	$\frac{-2457}{8520s + 1}e^{-5700s}$
blowline Kappa #	$\frac{-1.0}{7978s + 1}e^{-6900s}$	$\frac{-2.4}{8021s + 1}e^{-5900s}$	$\frac{-2657}{7675s + 1}e^{-7200s}$	$\frac{-2867}{7847s + 1}e^{-6100s}$	$\frac{-2448}{7793s + 1}e^{-8600s}$
Residual effective alkali	$\frac{-2827s - 0.14}{2.9e07s^2 + 10180s + 1}e^{-3200s}$	$\frac{-5678s - 0.32}{2.7e07s^2 + 9946s + 1}e^{-2300s}$	$\frac{501.2}{7675s + 1}e^{-520s}$	$\frac{980.3}{7944s + 1}e^{-500s}$	$\frac{1031}{7390s + 1}e^{-510s}$
Grade transition switch as disturbance					
Upper heater Kappa #	$\frac{4364s + 0.85}{3.9e6s^2 + 6846s + 1}e^{-1500s}$				
Lower heater Kappa #	$\frac{3662s + 1.2}{6174s + 1}e^{-2900s}$				
Extraction screen Kappa #	$\frac{2724s + 3.3}{6497s + 1}e^{-7700s}$				
blowline Kappa #	$\frac{1009s + 3.2}{6048s + 1}e^{-11000s}$				
Residual EA	$\frac{20290s + 0.21}{2.9e7s^2 + 9570s + 1}e^{-5800s}$				

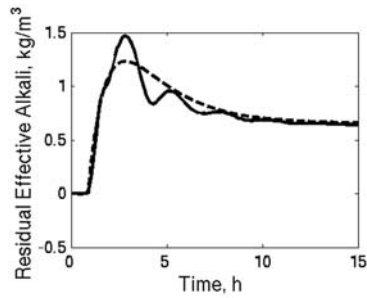


Figure 17.13. Identification of SOPTD + single zero using step test data generated by reducing upper heater temperature.

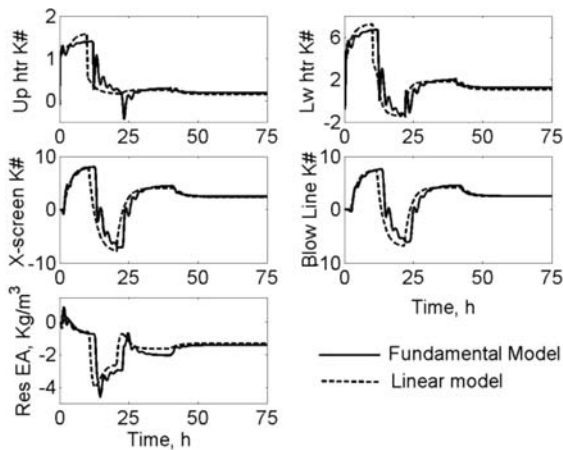


Figure 17.14. Validation of the identified linear model with fundamental model. The following inputs were implemented: (a) at $t = 2$ h, upper heater temperature, lower heater trim, and white liquor to top of digester changed by -5 K, $+40\%$, -10% respectively; (b) at $t = 20$ h, upper heater and lower heater temperatures changed by $+5$ K and $+4$ K, respectively; (c) at $t = 25$ h, upper heater trim and lower heater temperature changed by -20% , -4 K; respectively and (d) at $t = 45$ h upper heater trim changed by $+20\%$. The following nomenclature has been used: Up htr – upper heater; Lw htr – lower heater; X-screen – extraction screen; Res EA – residual effective alkali.

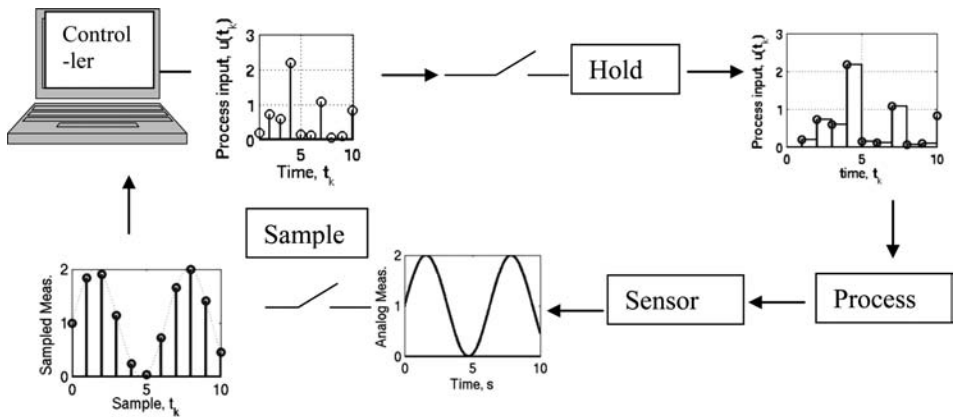


Figure 17.15. Sampled data system: conversion between the analog and discrete signals in a closed loop system.

For a general order system, the model assumes the following form:

$$x(k) = \sum_{i=1}^n a_i x(k-i) + \sum_{i=1}^m b_i u(k-i) \quad (17.21)$$

Often, the model parameters need to be identified from noisy data. To account for the noise in the data, the models have an additional term to include the noise effect:

$$x(k) = \sum_{i=1}^n a_i x(k-i) + \sum_{i=1}^m b_i u(k-i) + \sum_{i=0}^p c_i \xi(k-i) \quad (17.22)$$

where ξ represents white noise. Equation (17.22) is called Autoregressive Moving Average Exogenous process (ARMAX).

17.3.8 Discrete-time models for nonlinear processes

All simple models considered thus far are linear. If the process dynamics are severely nonlinear, it may be essential to use nonlinear approximate models. A few representative nonlinear discrete-time models are:

- (i) *Block oriented models*: These models consist of cascading linear and nonlinear blocks. In Hammerstein models, the input goes through a static nonlinear block followed by a linear dynamic block (Smith *et al.*, 2007). In case of Wiener models, inputs go through a linear dynamic block followed by nonlinear static block.
- (ii) *Laguerre polynomials*: These are approximations to the dynamics of both linear and nonlinear processes. The response $G(t)$ of a process to an impulse input can be described by using Laguerre functions $L_i(t)$ as the basis functions. Thus:

$$G(t) = \sum_{i=1}^{\infty} a_i L_i(t); \quad a_i = \text{coefficient}; \quad (17.23)$$

$$L_i(t) = \sqrt{2p} e^{-pt/2} \sum_{n=1}^{i+1} \frac{i!(-pt)^{(n-1)}}{(n-1)!(i-n+1)!}$$

Similarly, in s-domain, the transfer function of a system can be expressed as:

$$G(s) = \sum_{i=1}^{\infty} a_i L_i(s); \quad L_i(s) = \frac{(s-p)^{i-1}}{(s+p)^i} \quad (17.24)$$

where p is called the Laguerre pole. The coefficients a_i tend to decrease as i increase so that only N terms are required to approximate the transfer function (that is a finite impulse response). One can also work with a discrete version of a Laguerre network which is conceived as a cascade of N filters ($i = 1$ to N). The output of filter i is taken as $L_i(t)$. With a sampling period T , discrete model assumes the form (Zervos and Dumont, 1988):

$$L_i(k) = \sum_{j=1}^{i-1} a_{ij} L_j(k-1) + b_i u(k-1) \quad (17.25)$$

The output of the process is written as:

$$y(k) = a_0 + \sum_{i=1}^N a_i L_i(k) \quad (17.26)$$

For nonlinear processes, Dumont *et al.* (1994) has proposed the addition of a nonlinear term of the form given below to the above equation:

$$\sum_{i=1}^N \sum_{j=1}^N L_i(k) c_{ij} L_j(k) \quad (17.27)$$

This modeling formulation has been used by Saha *et al.* (1999) for modeling and optimizing control of continuous fermenter.

- (iii) *Neural networks*: A neural network is a connectionist network with one or more layers, with the i th layer containing n_i nodes. Each node j in layer i receives weighted signals from the outputs of the previous layer:

$$z_i^j = \sum_{k=1}^{n_{j-1}} w_{ik}^j x_k^{j-1}; \quad x_i^j = f(z_i^j), \quad x_i^j = \text{output of } j\text{th node in } i\text{th layer.} \quad (17.28)$$

Using data relating inputs and outputs, network weights w_{ik}^j ($j = 1, \dots, N, k = 1, \dots, n_{j-1}$) are obtained to get the best fit. In the model for ethanol fermentation (Bartee *et al.*, 2009), neural networks are used to model the conversion rates of dextrins, sugar and ethanol.

17.4 BASIC STRATEGIES FOR CONTROL

All control structures are governed by two basic control philosophies namely, feedback and feed forward. The basic philosophy of feedback control involves monitoring the current status of the process as indicated by the process variable called Controlled Variable (CV). Based on the departure of the current status from the desired status, the controller initiates corrective action by appropriately varying the Manipulated Variables (MV) to bring the process back to the desired status. The feedback control has two functions namely, (i) reject the effect of disturbances on CV (regulatory control), and (ii) move CV to track the variation in set point (servo control).

In the case of feedforward control, the disturbance variable is monitored and conveyed to a feedforward controller. Based on the knowledge of the process behavior, the feedforward controller estimates the effect of variation of disturbance on the CV and the change in MV needed to bring the CV back to set point. Since the control action is initiated at the onset of disturbance, its correction is instantaneous and more effective than feedback control, which fails to act until the effect of the disturbance manifests as change in CV. However, implementation of feedforward control requires a reasonable knowledge of process dynamic behavior. From the basic philosophy of feedback and feedforward control, various control structures have evolved. These could be classified into the following:

A. CONTROL OF SINGLE INPUT-SINGLE OUTPUT (SISO) PROCESSES

- 1) Single feedback loop
 - a) Linear PID controller – Fixed parameters or adaptive
 - b) Internal model controller
- 2) Single loop feedback controller with disturbance compensation
 - a) Cascade controller – input disturbance compensation
 - b) Feedback – feedforward controller – output disturbance compensation
 - c) Feedback controller with time delay compensation

B. MULTIVARIABLE CONTROL STRUCTURES FOR UNIT-WIDE CONTROL

- 1) SISO extensions to multivariable control
 - a) Decentralized SISO loops to minimize interaction effects
 - b) SISO Control with decouplers for interaction compensation
- 2) Model based multivariable controllers
 - a) Model Predictive Control

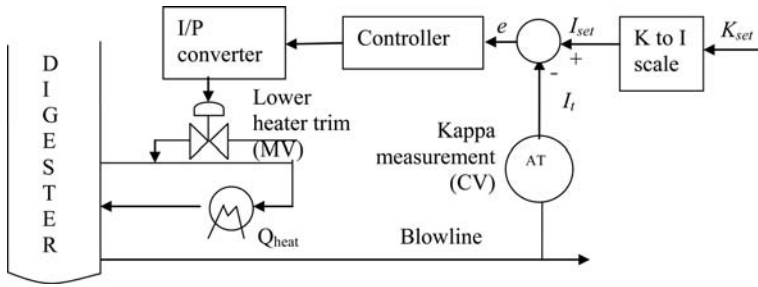


Figure 17.16. Process and instrumentation diagram (P&ID) depicting control of blowline Kappa number using makeup trim liquor stream to lower heater. AT: Kappa analyzer transmitter.

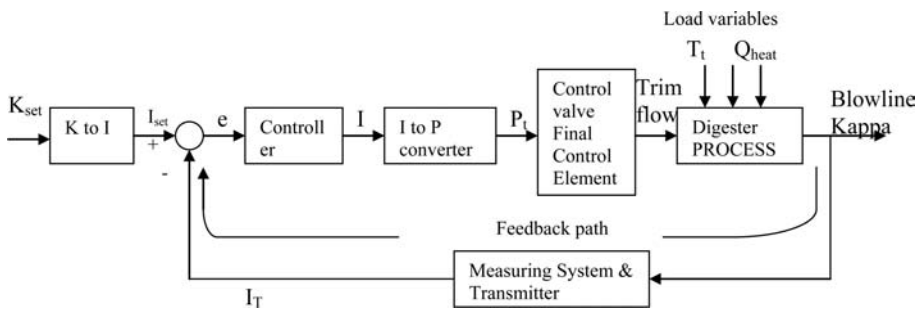


Figure 17.17. A block diagram representation of the closed loop shown in Figure 17.16.

- 3) Optimizing control structures
 - a) Hierarchical Steady State Optimization With Control
 - b) Dynamic Optimization

17.4.1 Single feedback loop control

Translation of the feedback strategy into an actual implementation framework is illustrated for the control of blowline Kappa number control using the lower heater trim flow as the MV (Fig. 17.16). We assume that the Kappa number measurement is available (CV), which is measured by a sensor transmitter AT whose output (I_t , mA) is compared with set point signal K_{set} transformed into I_{set} . The resulting error signal is sent to a controller whose output I (mA) is sent to a current-to-pressure I/P converter. The output of I/P converter P (kg/cm²) is sent to a pneumatic control valve. The control valve varies the flowrate of the makeup trim to the lower heater (MV).

The disturbances to the process are temperature of trim stream T_t , and heat input by the heater Q_{heat} . The disturbances are also called load variables. A block diagram of the P&ID above is shown in Figure 17.17, which provides information flow representation of the control problem. The controller is only a part of the overall hardware/software of the control loop. The controller typically uses the error signal to decide on how to operate the final control element, which in the current case is the control valve. The most widely used control algorithm used in single loop control is the Proportional-Integral-Derivative (PID) and it consists of the blend of three corrective components:

Proportional action: $K_c e$, which is based on instantaneous error e defined as, $e = \text{set point} - \text{value of CV}$. This action does not introduce dynamics in the loop.

Integral action: $\frac{K_c}{T_I} \int_0^t e \, dt$, which is based on cumulative effect of all past errors. Note that the integral term stops rising or falling only when the error goes to zero. It is the slowest of all since the integral reflects the history of the process. This action provides the steady state value of corrective action since P action and D action go to zero when the process reaches steady state and error is zero. The integral action introduces integrator dynamics in the loop.

Derivative action: $K_c T_D \frac{de}{dt}$, which is based on the rate of change of error and hence is faster than P or I actions, which depend only on the error and not its rate. The mathematical equation for the PID controller is as follows:

$$I = I_0 + K_c e + \frac{K_c}{T_I} \int_0^t e \, dt + K_c T_D \frac{de}{dt} \quad (17.29)$$

where K_c is called the proportional gain, T_I the integral time and T_D the derivative time. Most commercial manufacturers use the term proportional band (PB) instead of proportional gain and the two are related as follows:

$$PB = \frac{\text{maximum range of controller output}}{\text{maximum range of measured variable}} \times \frac{1}{K_c} \times 100 \quad (17.30)$$

Similarly the term reset rate is often employed, which corresponds to the reciprocal of the integral time. The various controllers for single loop control are listed below:

Proportional (P-only) Controller: The P-controller does not add dynamics to the control loop but can cause steady state errors (offset). Thus, it can be used in situations where offset is permissible, a common application being averaging control of level.

Proportional Integral (PI) Controller: Most widely used in situations where there are not too many lags in the system like flow control, pressure control, level control, and blending control in a single tank.

Proportional Integral Derivative (PID) Controller: Used in situations where there are many lags in the system like in thermal processes, distillation columns etc. The derivative action compensates to some extent the effect of process lags. In noisy processes, like flow, derivative action should never be used as derivative part of the controller amplifies high frequency noise resulting in erratic control actions.

Closed loop systems show a tendency for instability when controller settings are tightened to improve performance of control. This stability–performance trade-off is due to the inherent dynamics in the closed-loop system. Typically, stability issues become important when the dynamic elements in the loop exceed order two. Time delay also poses stability problems and lowers the level of achievable performance. Table 17.3 summarizes the closed loop stability for various orders of open loop systems.

Single loop controller with PID control becomes less effective under the following conditions:

- Multicapacity processes with large delay in responses.
- Time delay to major time constant ratio goes above 0.6.
- Need to handle disturbances which are too fast for the feedback loop.
- Process with large gain variation across the operating regime like *pH* process.

In the above cases, alternate control structures need to be used to overcome limitations of single loop PID control. An alternative strategy to PID controllers involve using an internal model to guide the controller design.

17.4.2 Internal model control structure

In internal model control, a process model $\hat{G}_p(s)$ is used as an internal model. As shown in the block diagram below (Fig. 17.18), the IMC controller design is based on a realizable inverse of the

Table 17.3. Stability characteristics of closed loop.

Process	Controller	Stability
First order	P	Stable at all values of K_c
	PI	Stable for all K_c and T_I
Second order	P	Stable but damping ratio decreases with increase in K_c
	PI	Prone to instability at high K_c or low T_I
Third order	P	Unstable at high value of K_c
	PI	Unstable at high value of K_c or low value of T_I
Higher order	P, PI	Unstable at high value of K_c or low T_I
	PID	Improves stability margin
Process with time delay	P, PI, PID	Unstable at high K_c and low T_I derivative action useful for lower time delay values

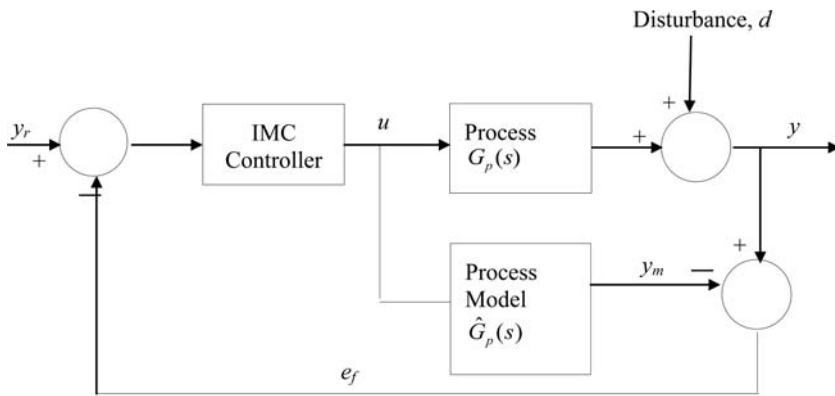


Figure 17.18. Block diagram representation of internal model control structure. Here the plant model mismatch is used as a feedback signal.

process model along with a filter that has the dual purpose of shaping the closed loop response and providing robustness to plant model mismatch. Internal model controller has certain structural similarities with the Smith Predictor scheme (see section 17.4.3).

The process output, in response to a control signal u , is given by $y = G_p u + d$. The signal u is also sent to a model of the process whose output is $y_m = \hat{G}_p u$. The feedback signal $e_f = y - y_m$ is sent to the controller. If the model matches the process exactly, this signal equals to the disturbance d . The IMC controller design is given by:

$$G_{IMC}(s) = G_{INV}(s)F(s) \quad (17.31)$$

where $G_{INV}(s)$ represents the invertible part of the model $\hat{G}_p(s)$. $F(s)$ is a low-pass filter that makes the controller transfer function rational and shape the nature of closed loop response. A common choice for F is the first order transfer function of unity gain. Thus:

$$F(s) = \frac{1}{\lambda s + 1} \quad (17.32)$$

An attractive property of the IMC controller is that so long as the steady state gain of the controller is identical to the reciprocal of the process model $\hat{G}_p$, an offset free control is obtained even if that $G_p \neq \hat{G}_p$. Table 17.4 summarizes the IMC control law and the equivalent PID controller

Table 17.4. Synthesis of IMC controllers for various model structures. Also shown are PID equivalents, where possible.

Model	Model Inverse	Closed loop model	Single loop IMC controller	Equivalent PID Controller		
				K_c	T_I	T_D
$\frac{K_p}{\tau s + 1}$	$\frac{\tau s + 1}{K_p}$	$\frac{1}{\lambda s + 1}$	$\left(\frac{\tau}{K_p \lambda}\right) \frac{\tau s + 1}{\tau s}$	$\frac{\tau}{K_p \lambda}$	τ	
$\frac{K_p e^{-Ls}}{\tau s + 1}$	$\frac{\tau s + 1}{K_p}$	$\frac{e^{-Ls}}{\lambda s + 1}$	$\frac{\tau s + 1}{K_p} \frac{1}{\lambda s + 1 - e^{Ls}}$	$\frac{\tau}{K_p(\lambda + L)}$	τ	
$\frac{K_p e^{-Ls}}{\tau s + 1}$	$\frac{\tau s + 1}{K_p(Ls + 1)}$		$\frac{\tau s + 1}{K_p(\lambda + 2L) \left[\frac{\lambda L}{\lambda + 2L} s + 1 \right]}$	$\frac{\tau}{K_p(\lambda + 2L)}$	τ	
$\frac{K_p e^{-Ls}}{\tau s + 1}$	$\frac{\tau s + 1}{K_p}$		$\frac{\left(\tau + \frac{L}{2}\right) \left(\frac{\tau L}{2(\tau + L/2)} s + 1 + \frac{1}{(\tau + L/2)s} \right)}{K_p(\lambda + L) \left[\frac{\lambda L}{2(\lambda + L)} s + 1 \right]}$	$\frac{\tau + L/2}{K_p(\lambda + L)}$	$\tau + \frac{L}{2}$	$\frac{\tau L}{2 \left(\tau + \frac{L}{2} \right)}$
$\frac{K_p e^{-Ls}}{\tau s + 1}$	IMC based Improved PI settings (Ogunnaike and Ray, 1994)			$\frac{\tau + L/2}{K_p \lambda}$	$\tau + \frac{L}{2}$	
$\frac{K_p}{(\tau_1 s + 1)(\tau_2 s + 1)}$	$\frac{(\tau_1 s + 1)(\tau_2 s + 1)}{K_p}$	$\frac{1}{\lambda s + 1}$	$\frac{(\tau_1 s + 1)(\tau_2 s + 1)}{K_p \lambda s}$	$\frac{\tau_1 + \tau_2}{K_p \lambda}$	$\tau_1 + \tau_2$	$\frac{\tau_1 \tau_2}{\tau_1 + \tau_2}$
$8 \frac{K_p e^{-Ls}}{(\tau_1 s + 1)(\tau_2 s + 1)}$	$\frac{(\tau_1 s + 1)(\tau_2 s + 1)}{K_p}$	$\frac{e^{-Ls}}{\lambda s + 1}$	$\frac{(\tau_1 s + 1)(\tau_2 s + 1)}{K_p \lambda s} \frac{1}{\lambda s + 1 - e^{-Ls}}$	No equivalent IMC – PID controller settings		
$\frac{K_p}{(\tau_1 s + 1)(\tau_2 s + 1)}$	$\frac{(\tau_1 s + 1)(\tau_2 s + 1)}{K_p}$	$\frac{1}{(\lambda_1 s + 1)(\lambda_2 s + 1)}$	$\frac{(\tau_1 s + 1)(\tau_2 s + 1)}{K_p(\lambda_1 + \lambda_2 s) \left(\frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2} s + 1 \right)}$	$\frac{\tau_1 + \tau_2}{K_p(\lambda_1 + \lambda_2)}$	$\tau_1 + \tau_2$	$\frac{\tau_1 \tau_2}{\tau_1 + \tau_2}$

IMC controllers for models (Row 3, 4 and 8) have PI/PID structure with a cascaded filter.

tuning parameters for a variety of control relevant models Morari and Zafiriou (1989). The value of the filter parameter λ depends on the major time constant and the desired dynamic response of the closed loop. It also determines the robust stability of the closed loop. As a rule of thumb the value of λ should be greater than the maximum of $1.7L$ or one fifth of the dominant time constant. As can be seen from Table 17.4, for lower order models, the IMC based PID controller parameters can be directly related to the process model parameters. Other tuning rules based on various closed-loop performance indices such as quarter decay ratio, minimum integral time average error are also available in literature (O'Dwyer, 2003).

17.4.3 PI control of lower heater Kappa and blowline Kappa number

The transfer function matrix relating the controlled and manipulated variables in Table 17.2 can be used for control system design. The basic control design consists of a single input single output (SISO) feedback loop system that ignores the interaction effects with other variables. Let us take the simplest case where the lower heater Kappa number (y_2) will be controlled using the upper heater temperature (u_1) and the control of blowline Kappa (y_4) number using the flowrate of the trim liquor to the lower heater (u_4). In the next section, we will discuss methods, which provide guidelines to determine pairings between the manipulated inputs with the outputs of the SISO loops.

Thus, the 2×2 subsystem is as follows:

$$\begin{array}{l} \text{Lower heater} \\ \text{Kappa \#} \\ \text{blowline} \\ \text{Kappa \#} \end{array} \begin{bmatrix} y_2 \\ y_4 \end{bmatrix} = \begin{array}{cc} \text{Upper heater} & \text{Trim liquor} \\ \text{temperature} & \text{flow} \\ \left[\begin{array}{cc} \frac{-5791s - 1.25}{8429s + 1} e^{-1100s} & \frac{-587.3s}{8268s + 1} e^{-8400s} \\ \frac{-1.0}{7978s + 1} e^{-6900s} & \frac{-2867}{7847s + 1} e^{-6100s} \end{array} \right] \begin{bmatrix} u_1 \\ u_4 \end{bmatrix} \end{array} \quad (17.33)$$

The P&ID showing the Kappa sensor on the blowline, which is used to determine the lower heater trim flow rate is shown in Figure 17.16. The block diagram representing the process and controller is shown in Figure 17.7. A similar P&ID and corresponding block diagram for control of the lower heater Kappa can be arrived at. For simplicity, the two controllers will directly change the manipulated variable without involving the I/P converter and the final control element. Both the controllers are tuned using the IMC based “improved PI” tuning rule with the closed-loop time constant λ chosen as 7000 and 9000 seconds for the respective loops. The control performance for control of individual transfer functions (namely g_{21} and g_{44} , in Table 17.2) are shown in Figure 17.19 for a set point change of 2 units. The large delays significantly limit the bandwidth of the closed loop system and the performance appears sluggish. Note also the derivative kick in Figure 17.19a. This occurs due to the presence of a zero in the process transfer function g_{21} .

Note that in the above simulation, although the outputs were based on the approximate models and in absence of interaction effects (that is, contribution of interactions by g_{24} and g_{41} were not simulated), the performance of the closed loop response is unsatisfactory. This is because large time-delays, as in the digester example, limit the efficacy of feedback.

17.4.4 Single-loop control with disturbance compensation

17.4.4.1 Input disturbances: cascade control

The single loop feedback control performance deteriorates when disturbances enter the process at a location with a slow dynamic path to the measurement point. In the control of blowline Kappa number, any changes in the upstream pressure of the makeup liquor to the lower heater will cause fluctuations in the manipulated inputs. Such disturbances that affect the MV are known as input disturbances. Thus, for the same signal to the valve a different quantity of trim may be injected,

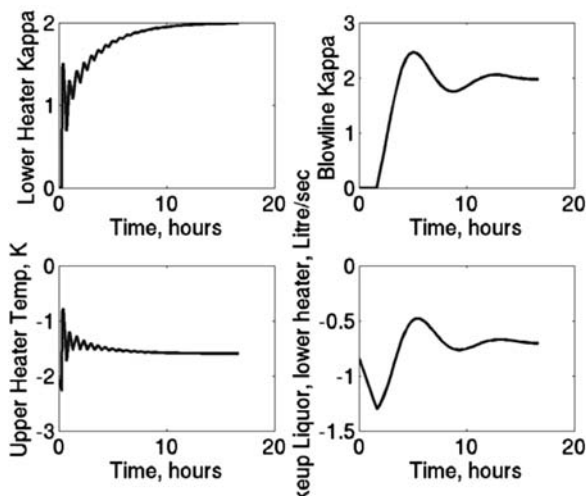


Figure 17.19. IMC-based PI control using the improved PI tuning rules. The two outputs have been simulated using the transfer function matrix in equation (17.33) without interaction.

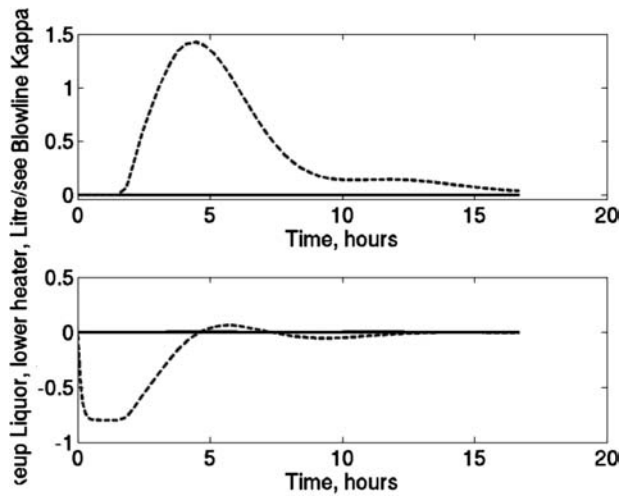


Figure 17.20. The dashed line indicates the excursions in Kappa number when a step disturbance enters the manipulated input, namely, makeup trim liquor. The solid line indicates the response when the cascade control strategy is implemented.

thus disturbing the operation. The effect of this disturbance is sensed only after it affects the blowline Kappa number and control action can be initiated only after the feedback signal reaches the controller. Making the controller tuning aggressive causes excessive overshoots in the CV because of the multi-capacity nature of the process and the overall disturbance rejection is slow. The dashed lines in Figure 17.20 show disturbance rejection by the PI controller (with the same tuning as reported in Fig. 17.19) when a step disturbance enters the makeup liquor to the lower heater at 0 hours. It is clear that the effect of the disturbance persists for a significant duration before the PI controller can eliminate it. Any change in trim liquor concentration is sensed only

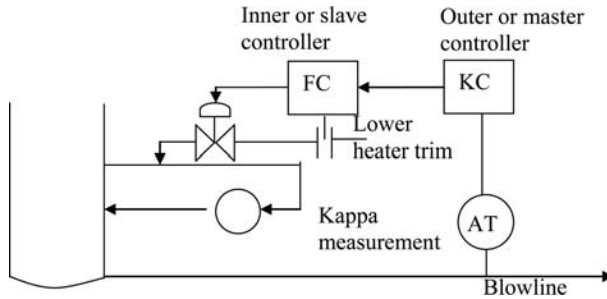


Figure 17.21. Implementation of cascade control for input disturbance rejection. The faster acting flow control loop rejects the disturbance, which therefore do not affect the slower outer loop. AT: Kappa analyzer transmitter; KC: Kappa controller; FC: flow controller.

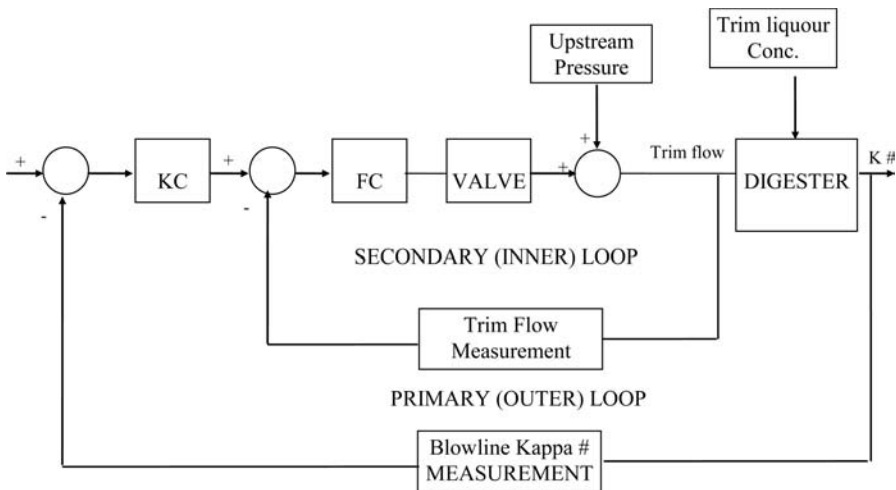


Figure 17.22. A block diagram representation of cascade control implementation.

after it affects the blowline Kappa number. Since the digester has larger capacitance affecting its response, its dynamics are comparatively slower.

Such disturbances can be more effectively compensated by including a flow sensor and an additional controller FC in a cascade fashion as shown in Figure 17.21. Here, the disturbances on the manipulated inputs are sensed by the flow measurement and rapidly compensated by the inner controller. The outer Kappa controller, KC, now provides set points to the flow controller and is not affected by these disturbances.

The corresponding block diagram is shown in Figure 17.22. Since the valve dynamics are significantly faster than the digester dynamics, changes in upstream pressure result in a change in the trim liquor flow rate with fast dynamics. Thus, the disturbance is locally compensated by the flow controller FC and does not propagate significantly to the digester. Set point changes demanded by KC occur at rates which are adequately handled by the faster inner loop controlled by FC.

The results for the case when the disturbance enters the lower heater trim flowrate using cascade control are shown as the solid line in Figure 17.20. Here the disturbances in the flowrate are measured and rapidly compensated by changing the valve position to achieve the desired flowrate. Since these disturbances do not enter the much slower outer Kappa loop, the output

remains unaffected by these disturbances. Thus, it is clear that the cascade control scheme is able to reject the disturbance before it affects the blowline Kappa.

Conditions suitable for implementation of cascade control are: (i) Inner loop is faster than the outer loop i.e. critical frequency of inner loop is much greater than that of the outer loop; (ii) Major load variable enters the inner loop. This situation exists in most of the cascade control loops where the inner loop is usually a flow control system and outer loop is a temperature, pressure or composition control loop. Cascade control is less effective for disturbances, which occur outside inner loop.

17.4.4.2 Output disturbances: feedforward–feedback control

While cascade control is effective for disturbances affecting the manipulated inputs, disturbances, which affect the plant output are appropriately handled in a feedforward control structure. In the digester example, any change in the white liquor concentration in the trim stream will affect the blowline Kappa number. A feedback controller will initiate corrective action only after an error is detected. However, if the change in the concentration can be measured or estimated, then the trim flow rate can be adjusted directly, so that the impact of the disturbance is not felt on the output. Thus, design of the feedforward controller requires process knowledge. In the digester example, this knowledge is encapsulated in terms of the transfer functions (Table 17.2) and can be represented as:

$$y(s) = G(s)u(s) + G_d(s)d(s) \quad (17.34)$$

where the first term captures the effect of the MV on the CV and the second term captures the effect of disturbance d . One can design a feedforward control law using the measurement of the disturbance to estimate the manipulated variable value, which will compensate for the disturbance thereby bringing the output to its target value (which, in terms of deviation variables, is zero). Thus;

$$u_{\text{feedforward}}(s) = -\frac{G_d(s)}{G(s)}d(s) = G_{FF}(s)d(s) \quad (17.35)$$

If the process and disturbance transfer functions are approximated with first order plus time delay models (Model 1), the feedforward controller $G_{FF}(s)$ becomes a lead lag element and takes the following form,

$$G_{FF}(s) = -K_{FF} \frac{\tau_s + 1}{\tau_d s + 1} e^{-\gamma s} \quad (17.36)$$

where the time delay in the lead-lag filter, γ , must always be greater than zero. Feedforward control is sensitive to errors in the transfer functions $G(s)$ and $G_d(s)$. Thus, feedforward is always augmented with feedback control as shown in Figure 17.23. The simulation result comparing the feedback control (dashed) structure with the feed forward–feedback control (solid) for a 5% step increase in the trim liquor concentration at 0 hours is shown in Figure 17.24. Conventional feedback control shows overcooking (smaller Kappa number) due to the increased concentration of the liquor. Subsequently, the feedback control acts upon the error signal and reduces the trim flow rate. However, in case of the feed forward–feedback control system, the feedforward component directly senses the change in the trim liquor concentration and compensates for the increased trim liquor concentration by reducing its flowrate. Thus, the effect on the blowline Kappa is insignificant.

17.4.5 Feedback control with time delay compensation: the Smith predictor

The presence of excessive time delay is seen to affect the performance of process control loops. One method proposed by Smith (Ogunnaike and Ray, 1994) is to have a prediction model, which informs the controller of the effect of its control action ahead of the actual response reaching the controller. This leads naturally to the structure shown in Figure 17.25. Taking aggressive control action will destabilize the significantly time-delayed system. This limitation can be overcome by

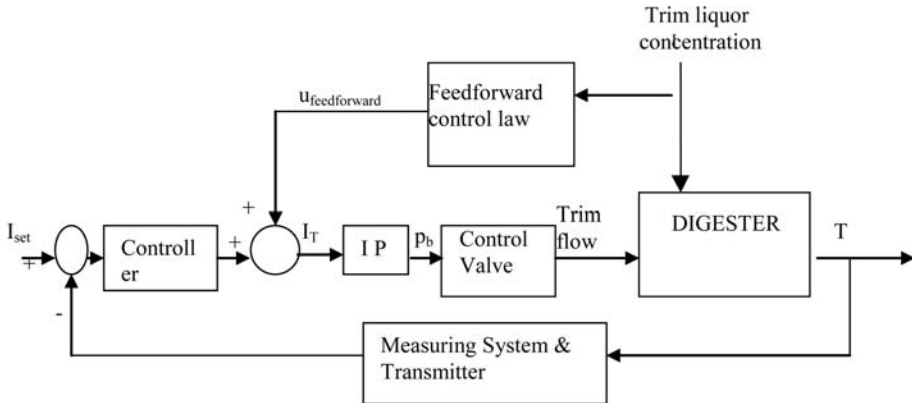


Figure 17.23. A block diagram representation showing implementation of feedforward control in addition to feedback control.

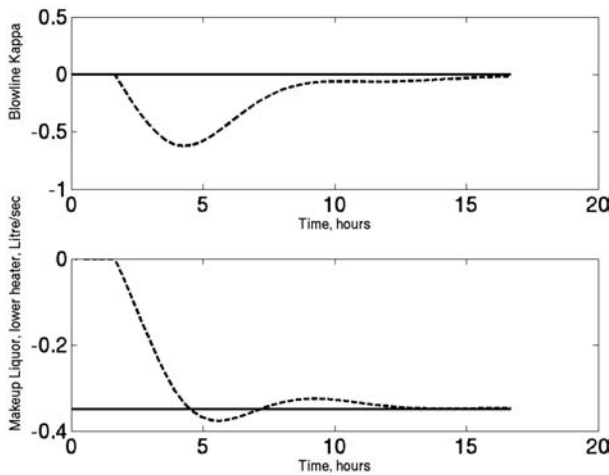


Figure 17.24. The dashed line indicates the feedback control performance when a 5% step increase in trim liquor concentration enters the digester as a disturbance. The feed forward-feedback system (solid line) measures the disturbance and estimates the reduction in the flowrate that should be affected to compensate for the increased concentration.

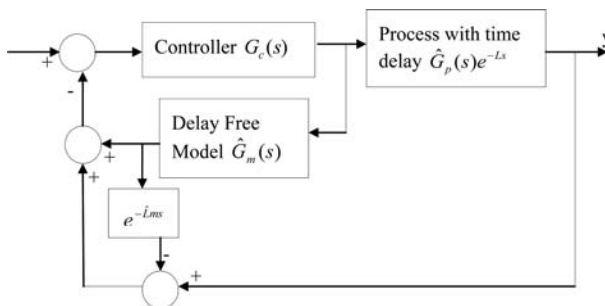


Figure 17.25. Smith predictor scheme. Subscript m refers to the model.

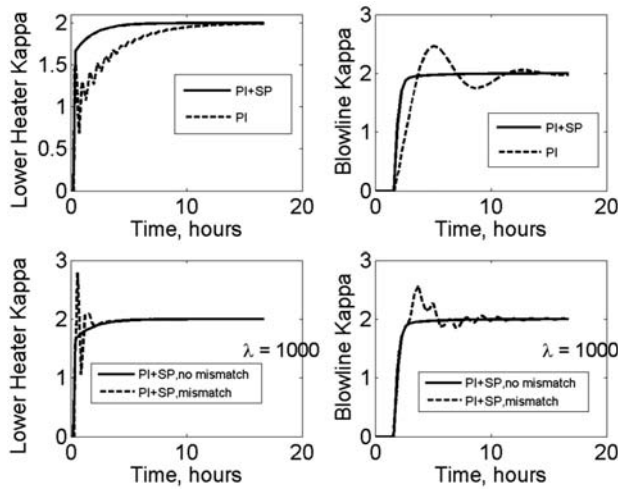


Figure 17.26. (a, b) Comparison of time delay compensation when using PI with time delay compensation using Smith predictor (solid line) with PI control (dashed). (c, d) show the deterioration of control performance when using imperfect knowledge of time delay (dashed line) relative to the case when perfect knowledge is assumed.

use of time-delay compensation. Here, a minor inner loop is provided that predicts the delay-free response and provides this information to the controller. Thus, the controller can be designed for the delay-free process model, $\hat{G}_p(s)$. As a result, the closed loop time constant can be reduced and the control tightened. If the model represents the process exactly, then the performance of the Smith predictor scheme can be expected to be significantly superior relative to the single loop controller.

Recall that the linear closed loop response in Figure 17.19 was observed to be sluggish and oscillatory. One reason for such behavior is the fact that the large size of the digester implies significant time delays (eq. 17.33). The transfer function matrix in Table 17.2 shows that the smallest time delays are of the order of 8 minutes (between residual EA and white liquor flow to top of digester) while the largest time delay is of the order 3–4 hours (between temperatures/flows on top of the digester and Kappa numbers at bottom of the digester). As can be inferred from the IMC-PI tuning rules, the presence of large time delays limits the controller gain and the closed loop system is sluggish. Figure 17.26a,b, shows the closed-loop response using a Smith predictor for a non-interacting system (solid line). Since the bandwidth limitation due to the delay is removed, the controllers could be aggressively tuned ($\lambda = 1000$ s). The results without using time-delay compensation are also shown for comparison (dashed line in Fig. 17.26a,b). However, as with feedforward controllers, the Smith predictor is based on a model and its performance is susceptible to modeling errors. In the case of a mismatch between the model used for Smith predictor design and the plant, the performance degrades. This effect is more pronounced when the model under-predicts the time delay. Figure 17.26c,d shows the effect of modeling errors on the performance of the closed-loop response. Here incorrect delays were provided for prediction (5000 instead of 6100 s and 800 instead of 1100 s). The deterioration in performance relative to perfect model (solid line) is apparent.

17.4.6 Single loop control with nonlinear compensation

A typical nonlinear control problem is the control of pH using the flowrate of the basic solution. pH control presents complexities because of the nonlinear neutralization characteristics (see

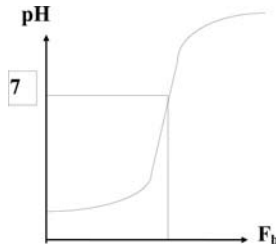


Figure 17.27. Neutralization characteristic curve depicts insensitive behavior at low or high pH with respect to the flowrate of the base, relative to the behavior at $pH = 7$.

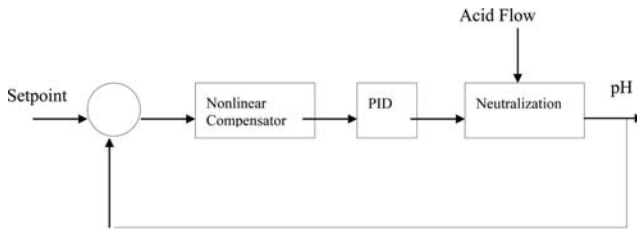


Figure 17.28. PID control with nonlinear compensation.

Fig. 17.27). The control problem becomes more acute when the pH control problem involves strong acid/strong base neutralization. There is a sharp change in the process gain, which becomes very high at $pH = 7$. A PID controller with fixed tuning parameters cannot be expected to give uniformly good closed loop performance over the range of pH variation. The controller gain has to be reduced to accommodate the high process gain in the vicinity of $pH = 7$ so that the closed-loop gain is at a desired value. When there is a disturbance, which pushes the pH to values away from 7, the gain reduces progressively and the controller gain is no longer large enough to effect a large change in the manipulated variable. This results in large pH deviations from the setpoint. A simple option to overcome this difficulty is to use a nonlinear compensator ahead of the PID controller. This compensator is the inverse of the neutralization curve. Other approaches involve online identification of nonlinear model and retuning of the PID controller based on the updated model parameters resulting in an adaptive control system.

17.5 UNIT-WIDE OR MULTIVARIABLE CONTROL

Control of a process unit such as the digester, bioreactor, paper machine or a distillation column is known as unit operations control, wherein n multiple controlled variables (CV) characterizing the unit operations are regulated by simultaneously varying m multiple manipulated variables (MV). Usually, the MVs outnumber the CVs resulting in positive degrees of freedom, that is, $m \geq n$. For such multivariable control problems, two approaches are commonly used: (i) decentralized control, which consists of multiple single variable control loops, or (ii) a centralized multivariable control approach.

17.5.1 Decentralized approach

In a decentralized approach, the n individual SISO loops are designed while ignoring interaction from the other loops. However, the manipulated variable, MV_i assigned for control of CV_i may also

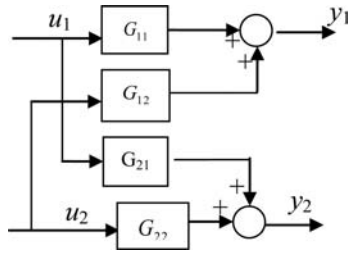


Figure 17.29. Block diagram showing multivariable interaction.

affect some or all other controlled variables. Thus, prior to the design of the decentralized SISO loops, the following issues must be addressed:

- What should the CV–MV pairing be that will cause the least interaction among the control loops?
- In strongly interacting systems, how can we design a decentralized structure, which actively compensates for the multivariable interactions?

To address the above issues, one needs to have a measure of multivariable interaction.

17.5.1.1 Measures of multivariable interaction: relative gain array (RGA)

RGA, proposed by Bristol (1966), is a measure to assess the extent of interaction. The relative gain $\lambda_{i,j}$ between the i th output or CV and the j th input or MV captures the extent of open-loop interaction between CV_i and MV_j when all other loops are closed. Thus, the interaction between CV_i and MV_j will include the effect of other controllers, which are provoked to ward off the effects of changes in MV_j . Thus,

$$\lambda_{ij} = \frac{\text{Gain between } CV_i \text{ and } MV_j \text{ with all loops open}}{\text{Gain of } MV_j - CV_i \text{ Path with all other loops closed except for } MV_j - CV_i} \quad (17.37)$$

Consider the 2 input-2 output process shown in Figure 17.29, which represents the open-loop block diagram whose transfer function matrix takes the form of equation (17.33).

Using the definition in equation (17.37), one can easily show that for the 2×2 system:

$$\lambda_{11}(\omega) = \frac{1}{1 - \frac{G_{12}(\omega)G_{21}(\omega)}{G_{11}(\omega)G_{22}(\omega)}} \quad (17.38)$$

where ω captures the frequency dependence of the relative gain. By construction, it can be shown the sum of all elements in a given row or column equals unity. Values of λ_{ij} lying between 0.8 and 1.2 indicate low interaction and thus a good candidate for pairing the i th CV and j th MV. High and low values of λ_{ij} imply severe interaction and the corresponding pairing should be avoided if possible. A loop should never be closed using a CV–MV pair which shows a negative relative gain.

Although, it is common to use the steady-state gain in computation of the RGA, that is, $\omega = 0$, it may not accurately represent the interactions caused by dynamic effects. Dynamic RGA, using various values of ω , is often more meaningful for systems with large time constants and delays. Often the RGA is calculated at the cross-over frequency at which the open loop phase is -180° .

Table 17.5. Input/output pairings used for decentralized controllers.

Controlled variable	Manipulated variable
Upper heater Kappa number	Make up liquor to upper heater
Lower heater Kappa number	Upper heater temperature
Extraction screen Kappa number	Lower heater temperature
Blowline Kappa number	Make up liquor to lower heater
Residual effective alkali	White liquor flow to top

17.5.1.2 Interaction analysis for the single vessel digester

The RGA for the 5×5 digester control problem, outlined in Table 17.2, is calculated at three different frequencies as shown below:

$$\begin{array}{c}
 \omega = 0 \\
 \begin{bmatrix} 15.8 & 0.0 & -24.9 & 0.0 & 10.1 \\ -18.7 & -11.5 & 55.4 & 7.6 & -31.7 \\ -3.7 & -24.7 & 48.8 & 45.3 & -64.7 \\ 7.3 & 35.8 & -82.5 & -55.9 & 96.3 \\ 0.3 & 1.4 & 4.2 & 4.0 & -9.0 \end{bmatrix}
 \end{array}
 \quad
 \begin{array}{c}
 \omega = 1 \times 10^{-8} \text{ rad/s} \\
 \begin{bmatrix} 0.6 & 0.0 & 3.2 & 0.0 & -2.8 \\ 0.2 & 6.3 & -6.8 & -7.9 & 9.2 \\ 4.2 & 7.5 & -16.8 & 10.3 & -4.2 \\ -4.2 & -13.3 & 23.1 & 0.2 & -4.8 \\ 0.1 & 0.6 & -1.7 & -1.6 & 3.6 \end{bmatrix}
 \end{array}$$

$$\begin{array}{c}
 \omega = 100 \\
 \begin{bmatrix} 1.0 & 0.0 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\ 0.0 & 1.0 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 4.2 & -3.2 \\ 0.0 & 0.0 & 0.0 & -3.2 & 4.2 \end{bmatrix}
 \end{array}
 \times$$

From the RGA data, the following observations are made:

- Some of the pairings based on the steady state RGA are not physically meaningful. For example the RGA ($\omega = 0$) suggests that use of upper heater temperature be used to control blowline Kappa ($\lambda_{41} = 7.28$). However, this pairing would be rejected on the physical grounds that the spatial separation between these two (see Fig. 17.3) induces a large transport lag of 115 minutes.
- The RGA ($\omega = 100$) and the RGA ($\omega = 1 \times 10^{-8}$) together give a reliable basis for arriving at the CV-MV pair. Although RGA ($\omega = 100$) suggests that the lower heater Kappa number should be controlled by the makeup liquor supplied to the upper heater, we reject this pairing since the corresponding element in the RGA ($\omega = 1 \times 10^{-8}$) is negative. Table 17.5 summarizes the input-output pairings based on the above dynamic RGA analysis.

Post-pairing analysis uses the Niederlinks Index to check for inherent stability in the control structure arrived after determining the pairing. Another measure to study stability is the Morari Integral Criteria which are popular (Yu and Luyben, 1986). For tuning of the PID controllers in the decentralized loop, a Biggest Log Modulus (BLT) tuning approach has been proposed by Luyben (1990). After the control loops are designed, measures like relative disturbance gain array (Stanley *et al.*, 1985) are available to evaluate the disturbance rejection capability of the chosen pairings. While interaction analysis aids in selection of pairings that will minimize interactions, active interaction compensators attempt to eliminate out the effects of interactions.

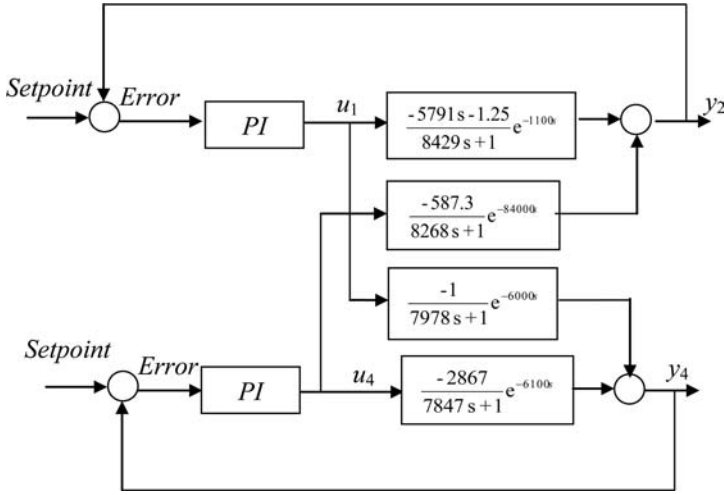


Figure 17.30. Block diagram depicting SISO loops in presence of multivariable interactions. The manipulated inputs determined by one controller acts as disturbance on other loops.

17.6 MULTIPLE SINGLE LOOP CONTROL USING INTERACTION COMPENSATORS: DECOUPLER DESIGN

Figure 17.30 shows two SISO loops, which interact with each other. A decoupler is an additional control element that actively cancels the effect of interactions. Theoretically, the transfer function for the decoupler, $D(s)$ could be the inverse of the process model so that the combined effect of the decoupler will yield the identity matrix:

$$D(s)G_p(s) = G_p^{-1}(s)G_p(s) = I \quad (17.39)$$

Now each control loop will act as independent SISO loops and each controller under the decoupled mode can be designed by ignoring interaction effects. However, there are problems in using an inverse of the process model because of realizability and implementation issues. It is easier to effect decoupling through a design, which cancels out only the interaction effect resulting in a simpler controller design.

It can be shown that for a 2×2 system, the MV injected to the system is modified by the decoupler as:

$$\begin{bmatrix} \Delta u_1 \\ \Delta u_2 \end{bmatrix} = D \begin{bmatrix} \Delta I_1 \\ \Delta I_2 \end{bmatrix} = \begin{bmatrix} 1 & -\frac{G_{12}}{G_{11}} \\ -\frac{G_{21}}{G_{22}} & 1 \end{bmatrix} \begin{bmatrix} \Delta I_1 \\ \Delta I_2 \end{bmatrix} \quad (17.40)$$

where ΔI_1 and ΔI_2 indicate the response from the SISO controllers prior to the decoupler. Then the effect of the decoupled controller input is to decouple the system as:

$$\begin{bmatrix} \Delta y_1 \\ \Delta y_2 \end{bmatrix} = \begin{bmatrix} G_{11} & 0 \\ 0 & G_{22} \end{bmatrix} \begin{bmatrix} \Delta I_1 \\ \Delta I_2 \end{bmatrix} \quad (17.41)$$

Very often, static decoupling is used which makes use of only the steady-state gains of the system. Decoupling is widely used in a number of applications. This has been used effectively in the control of a paper machine involving two controlled variables namely basis weight and moisture content.

Table 17.6. Summary of case studies with advanced strategies of SISO control.

Case Detail	Closed loop time constant, λ (s)		Response
	CV1	CV2	
Case 1: PI controllers designed without considering interaction	7000	9000	Fig. 17.31a,b. Lower heater Kappa shows highly oscillatory response. Blowline Kappa has relatively lower magnitude oscillations. However both oscillations are at very high frequency.
Case 2: PI controllers detuned to account for interaction	10,000	9000	Fig. 17.31c,d (solid line). Detuning reduces the oscillatory nature of response, but at the expense of speed of response, that is, a sluggish response is observed. Dashed line shows response if system is non-interacting (that is, interacting transfer functions in Fig. 17.30 are set to 0).
Case 3: PI controllers + Smith predictor	1000	1000	Fig. 17.32a,b (dotted line). The adverse effects of time delay are effectively addressed by the Smith predictor resulting in the ability to decrease λ to 1000 s and the consequent faster response.
Case 4: PI controllers + static decoupler + Smith predictor	1000	1000	Fig. 17.32a,b (solid line). Use of a static decoupler along with a Smith predictor yields a faster, non-oscillatory response.

17.6.1 Decoupler design for single vessel digester

Figure 17.30 shows the interaction effects of the 2×2 digester system for control of lower heater and blowline Kappa using the recommended MVs. The transfer function elements obtained from equation (17.33) were used as plant outputs. Four cases were studied for control of the plant that included the interaction effects. In Case 1, PI controllers were designed by ignoring interaction effects and were discussed in section 17.4. The debilitating effect of interactions is addressed in Case 2 by detuning the IMC based PI controllers achieved by increasing the filter parameter λ . The results are summarized in Table 17.6 and Figure 17.31, 17.32. Clearly, while detuning the controllers is an alternative (Case 2), the response is sluggish.

Use of Smith predictor and decouplers (Case 3) enable aggressive tuning by reducing the closed loop time constant in the IMC based improved PI design. The time-delay compensated closed loop response can be further improved by use of decoupling (Case 4). This is because interaction and delay compensators “inform” the controllers of likely delays and interactions due to the actions of the other controllers.

17.7 MODEL PREDICTIVE CONTROL: A MULTIVARIABLE CONTROL STRATEGY

Unlike the previous single variable control strategies, model predictive control (MPC) is a multi-variable approach, which inherently provides time-delay as well as interaction compensation. This is because it treats all CVs and MVs simultaneously and is therefore a multivariable controller and is thus well-suited to control process units involving a large number of controlled and manipulated variables. One of the advantages of MPC is its inherent ability to handle constraints as a part of formulation of the control law. The control law itself is computed as a result of an optimization exercise. MPC uses a prediction model to predict the behavior of the process over a future horizon using information about the present/past values of input $u(k)$, output $y(k)$ and disturbance $d(k)$

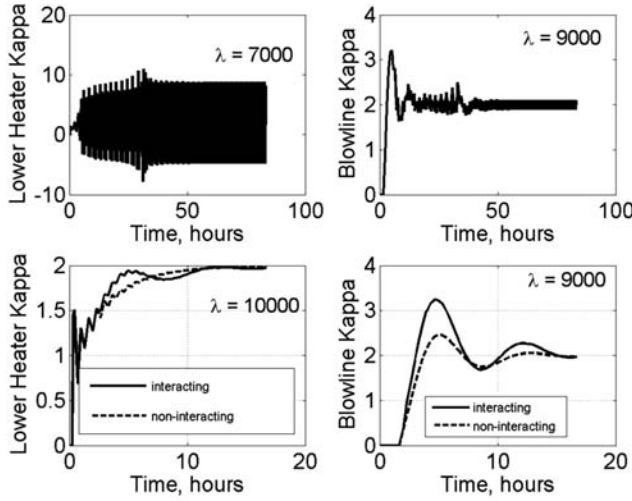


Figure 17.31. (a), (b) Performance of SISO loops in presence of multivariable interaction; (c), (d) performance of detuned SISO loops in presence of multivariable interaction (solid) and if no interactions existed between the two loops (dashed).

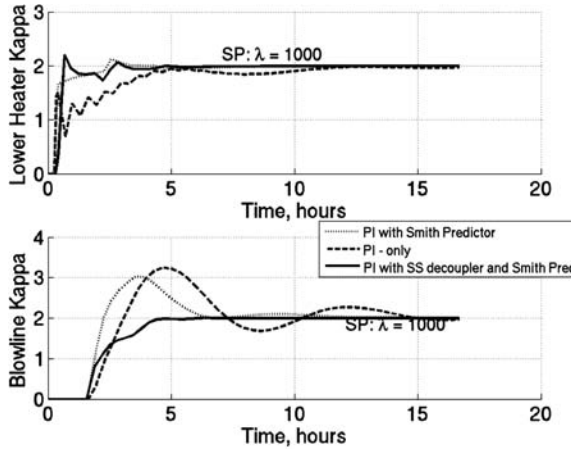


Figure 17.32. Use of Smith predictor along a steady state decoupler (solid) significantly improves performance in presence of multivariable interactions.

(either measured or estimated) (Fig. 17.33). The controller makes use of an explicit process model to forecast the future behavior of the plant, $Y_m(k+i)$ over the prediction horizon based on past inputs. It then calculates control inputs over a shorter control horizon that minimizes the deviation of the process trajectory from the set point trajectory $\gamma(k+i)$ over the prediction horizon while satisfying constraints. Thus, at each sample k , the following optimization problem is solved:

$$\min \sum_{j=1}^p (\gamma_{k+j} - y_{k+j})^T Q (\gamma_{k+j} - y_{k+j}) + \sum_{j=0}^{N-1} (u_{k+j}^T R u_{k+j} + \Delta u_{k+j}^T S \Delta u_{k+j}) \quad (17.42)$$

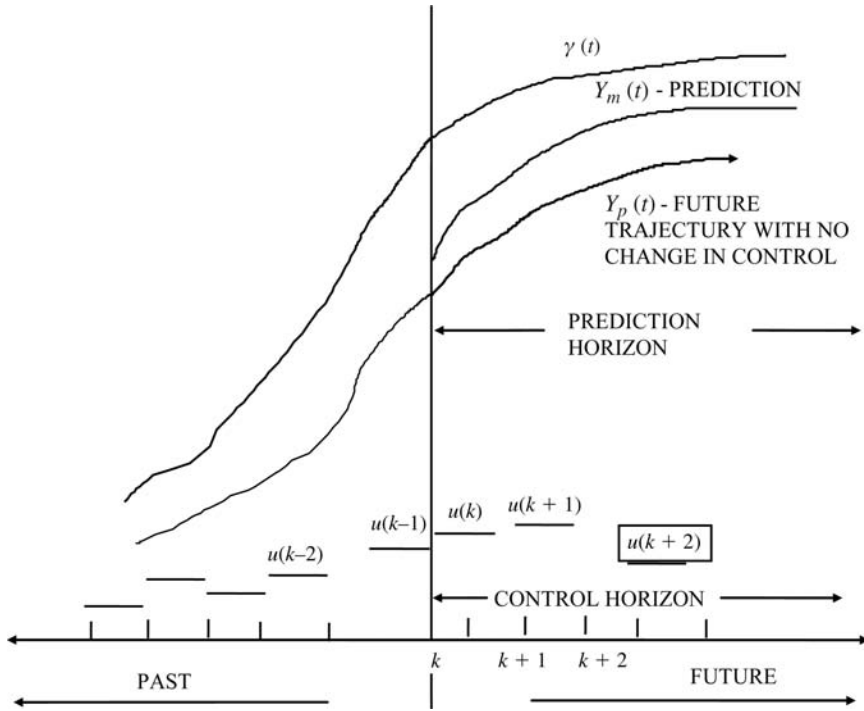


Figure 17.33. Schematic showing the receding horizon philosophy of model predictive control.

subject to the following constraints:

$$\begin{aligned}
 y_{\min} &\leq y_{k+i} \leq y_{\max}, & \forall i \in 1, \dots, p \\
 u_{\min} &\leq u_{k+i} \leq u_{\max}, & \forall i \in 1, \dots, N-1 \\
 \Delta u_{\min} &\leq \Delta u_{k+i} \leq \Delta u_{\max}, & \forall i \in 1, \dots, N-1 \\
 \text{and } u_{N-1} &= u_N = \dots = u_p
 \end{aligned}$$

where Q represents the penalty on the output deviation from the set point, and R and S represent the penalties on the inputs and the rate of change of inputs. The prediction and control horizons are represented by p and N , respectively. Though N future control moves, $u(k)$, $u(k+1)$, $\dots$, $u(k+N-1)$ are calculated at time step k , only the first move will be applied. In a moving horizon approach, the optimization problem is solved again at time step $k+1$, by incorporating the new measurement at $k+1$ to get the next set of future moves. This is also known as receding horizon control. At every sample, k , the model is updated using the available measurement. A large prediction horizon improves stability of the closed loop. It is recommended that the prediction horizon should be at least as large as the settling time of the process. If control horizon N is small, it leads to sluggish response. If a process has unstable modes, low N can cause runaway due to lack of adequate control moves. The move suppression parameter S can be used to suppress aggressive control action. MPC has a number of tuning parameters. Agachi *et al.* (2006) have provided the following guidelines:

- Prediction horizon p : Large p improves stability, minimum value of p should equal open loop settling time + control horizon; p should be larger than the closed loop settling time.
- Control Horizon, N : $N=1$, causes sluggish response, $N=4$ is a value often used.

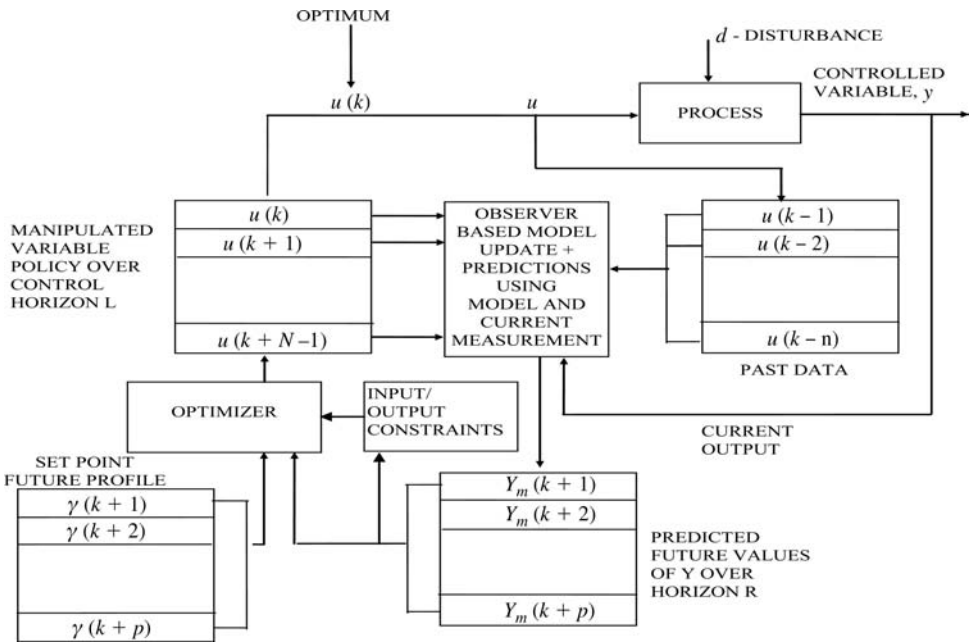


Figure 17.34. A schematic showing the computational aspects of MPC.

- S is a tuning parameter which can be used to restrain aggressive control moves and provide stability to MPC loop.

Tuning guidelines have also been provided by Shridar and Cooper (1997). MPC has been applied successfully for control of processes like pulp digester, bleaching plant, slaker, lime kiln and fermentation processes like fuel ethanol fermentation. The structure of the MPC algorithm can be represented as in Figure 17.34. Note that the current measurement is feedback to the model to enable online updating of the model and thus address model-plant mismatch (this is typically achieved using an observer such as the Kalman filter). Thus, MPC requires an online solution of a constrained optimization problem. However, to meet computational requirements, linear models such as shown in Table 17.2 are commonly employed. Here, the constrained optimization problem takes the form of a quadratic program for which efficient solvers exist. If the process is significantly nonlinear, then one may use nonlinear models, which, however requires an online solution of a nonlinear program.

17.7.1 Linear model predictive control for the single vessel digester

All control strategies presented so far were synthesized using the linear model and the control performance evaluated on the identified linear system itself. However, the plant is better described by the set of nonlinear differential equations of the first principles model rather than the linear transfer function models. Two control strategies were explored for control of the Kappa number profile, namely a decentralized PI scheme consisting of 5 SISO loops using the pairings of Table 17.5 and a centralized, linear constrained model predictive controller using linear models (Garcia and Morshedi, 1986) as shown in Table 17.2 (Bhartiya and Doyle, 2002). A nonlinear MPC control solution is reported in Padhiyar *et al.* (2006a). Feedback information was implemented by attributing the plant-model mismatch at sample k to a disturbance on the output and which is

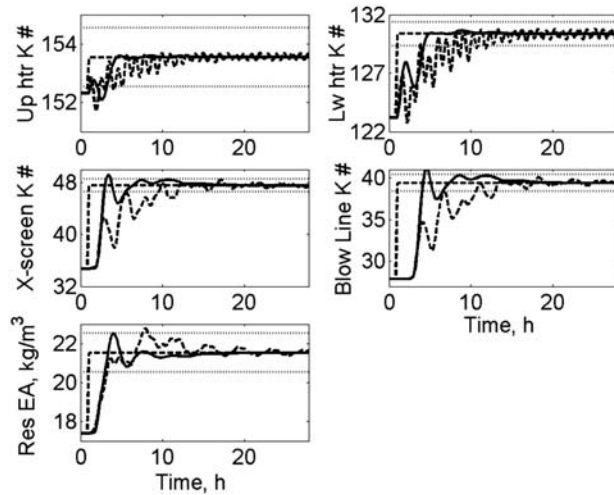


Figure 17.35. Outputs for set point change example using MPC (solid) and PI (dash) controllers. The digester was initially controlled at the following set points: (152.3 123.2 34.7 27.9 17.4) for the upper heater Kappa number, lower heater Kappa number, extraction screen Kappa number, blowline Kappa number, and the residual effective alkali [kg/m^3]. The new set points implemented after 1 hour of operation are as follows: (153.5 130.4 47.5 39.4 21.5).

constant over the prediction horizon. Both schemes use a 10-minute sampling interval. “Improved” PI IMC tuning rules were employed. The 5 input $\times$ 5 output linear MPC controller used the following tuning parameters during control simulations:

- prediction horizon, $p = 60$ samples (10 hours)
- control horizon, $N = 10$ samples (100 minutes)
- output weights, $\mathbf{Q} = \text{diag}((0.03 \ 0.03 \ 0.08 \ 0.09 \ 0.03))$
- input move suppression weights, $\mathbf{S} = \text{diag}((20 \ 20 \ 20 \ 20 \ 20))$.

The transfer function matrices were scaled using maximum expected magnitudes of deviations in the manipulated inputs and outputs enabling meaningful selection of weight matrices.

17.7.2 Control results and discussion

Case I: Servo Control Problem: As a first example, linear MPC using models in Table 7.2 and PI controllers were implemented for a set point change in the Kappa profile (characterized by the four measurements) and residual EA. This situation is often encountered while attempting to increase fiber yield. The first principles model discussed in section 17.2.1.2 was used as plant. Results are shown in Figures 17.35 and 17.36. The MPC controller (solid line) quickly responds to the set point change and drives all four measurements to the vicinity of the set points. The PI controllers for Kappa number control at upper and lower heaters were tuned aggressively, while the other three PI controllers were sufficiently detuned to avoid a ringing response. Detuning of upper and lower PI controllers causes very sluggish performance of the downstream controller. Settling times for the blowline Kappa number with the linear MPC and PI controllers are seen to be 6 h and 12 h, respectively. The sluggish response of the PI controller is a necessary consequence of large dead-times in the process. Use of time-delay compensation may provide one possible remedy. Figure 17.36 also suggests that there exists an apparent multiplicity of steady state solutions, that is, different combinations of the manipulated inputs yield identical values of the outputs. This fact is reflected in the poor conditioning of the steady-state gain matrix. For example, the Kappa

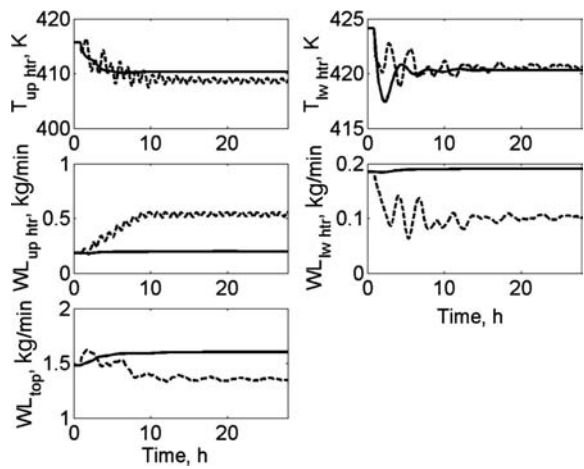


Figure 17.36. Manipulated inputs for set point changes depicted in Figure 17.10 using MPC (solid) and PI (dash) controllers.

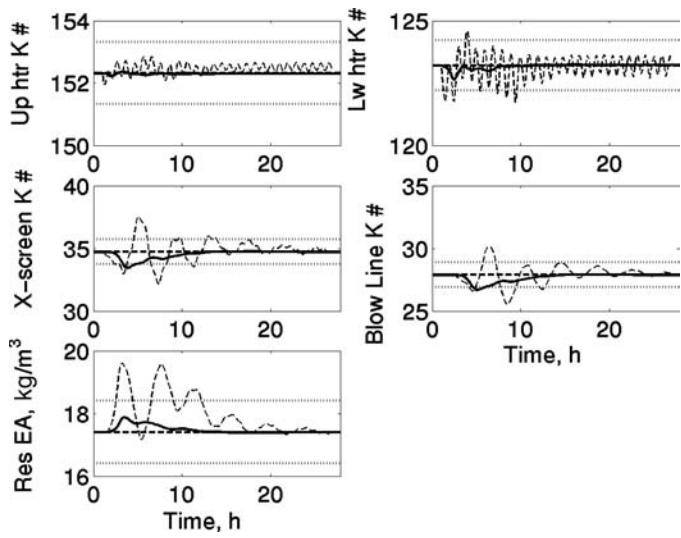


Figure 17.37. Outputs for disturbance rejection example using MPC (solid) and PI (dash) controllers. The disturbance is in the form of a step change in effective alkali of the white liquor stream from its initial value of 78.8 to 80.4 kg/m³ after 1 hour of operation.

numbers at the extraction screen and blowlines have similar gains and time constants but differ widely in the transport delay.

Case II: Regulatory Control Problem: The second example deals with rejection of unmeasured disturbance in the form of a 2% step increase in white liquor EA (Fig. 17.37). This disturbance affects both the make-up white liquor streams as well as that entering at the top. The long time required (> 10 hours) by the linear MPC controller to completely reject the deterministic disturbance is attributable partially to the fact that output feedback provides a poor estimate of unmeasured disturbances entering in the input as in the current case. However, the linear MPC controller outperforms those of the PI controller, which shows oscillatory behavior.

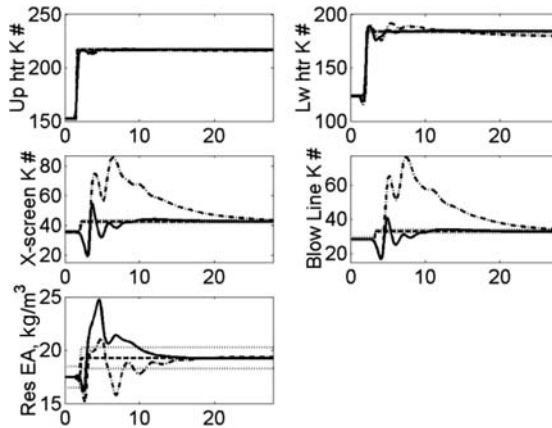


Figure 17.38. Grade transition control during a feedstock swing from hardwood to softwood using MPC (solid) and PI (dash-dot) controllers. The PI controller had to be severely detuned to avoid digester plugging.

Case III: Grade Transition Problem: The final example presents Kappa number profile control during a feedstock grade change from hardwood to softwood. As suggested in Doyle *et al.* (2001), grade transition is considered as a feedforward disturbance triggered by a binary switch. The corresponding transfer function models are shown in Table 17.2 and were used as the measured disturbance model in MPC. Set point changes were implemented only after the transition front reached the appropriate locations. For example, the lower heater Kappa number set point was changed after the transition front reached the lower heater location. Simulations results using both, PI and linear MPC controllers as tuned above reveal occurrence of digester plugging during a transition between hardwood and softwood (results not shown). The linear MPC controller with a 10-hour prediction horizon anticipates the large magnitude disturbance (change in blowline Kappa number due to grade change ≈ 155) and begins to take aggressive corrective action by increasing the flow rates and temperatures. However, these changes in liquor flows are felt almost instantaneously downstream by the old grade resulting in overcooking. The consequence is a situation of incipient plugging of digester, characterized in the model by a sharp decrease in the liquid content at the location of plugging (this is also known as dewatering of the digester). A consistent experience within the pulp and paper industry is that hardwood to softwood transitions are considerably more difficult than *vice-versa*. To avoid digester plugging during simulations, both, the MPC and PI controllers were detuned (reducing error penalty for linear MPC, and increasing closed-loop time constant for PI). Simulation results with the detuned controllers are shown in Figures 17.38 and 17.39. The MPC controller shows superior performance for control of blowline Kappa number. Figure 17.40 presents plant model-mismatch or errors in prediction of the five controlled variables by the linear model used in MPC. Prediction of blowline Kappa number shows large steady state errors in excess of 30. However, use of output feedback ensured offset-free control. Figure 17.41 shows axial compaction profiles (i) at start of grade transition, (ii) when the transition front has reached the extraction screens, and (iii) after the transition front has exited from the digester. As discussed previously the compaction profile shows a kink when the transition front reaches the extraction screen (that is the digester is filled with hardwood below extraction screen and with softwood above). Thus, during transition from hardwood to softwood, the digester approaches plugging-like conditions. In the failed grade transition scenario discussed above, aggressive control action caused the compaction in the vicinity of the extraction screens to become near-zero, indicating digester plugging. These simulations reveal that taking aggressive control action in anticipation of grade transition between hardwood and softwood can potentially

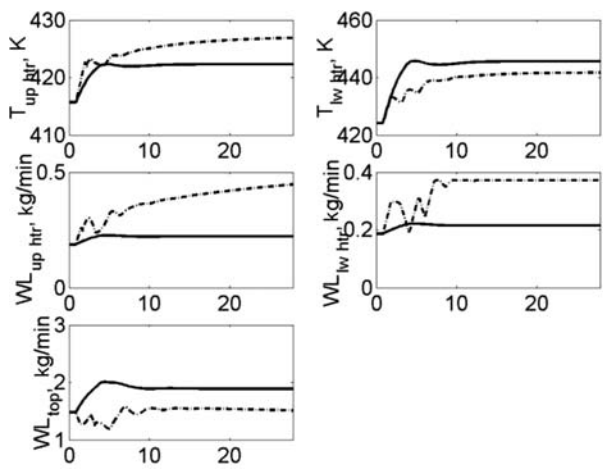


Figure 17.39. Manipulated inputs for hardwood to softwood grade change using MPC (solid) and PI (dash-dot) controllers.

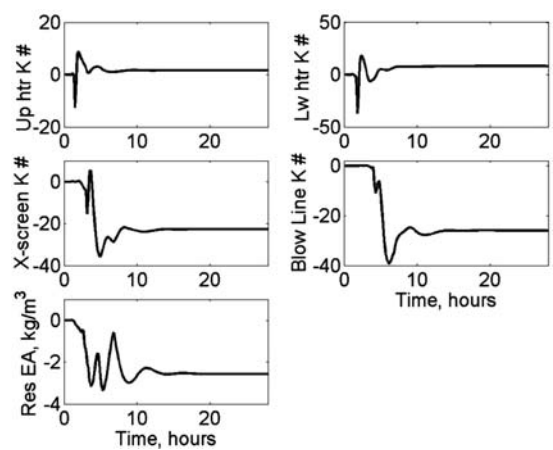


Figure 17.40. Plant-model mismatch evaluated as (plant measurement – linear model prediction). The linear model used by the MPC controller shows poor predictive ability during the hardwood to softwood feedstock grade transition.

plug the digester. An alternative is to avoid taking control actions until the transition front is well inside the digester. However, such a strategy will lead to production of large quantities of off-specification pulp. Integral absolute errors and settling times of the two controllers for the three simulation cases are summarized in Table 17.7.

17.8 REAL-TIME OPTIMIZATION

Optimization uses the degrees of freedom available in a process to attain performance goals like maximum profit/maximum throughput, minimum energy consumption, etc. When it needs to be done on a continuous basis, it sets the context for implementation of Real Time Optimization

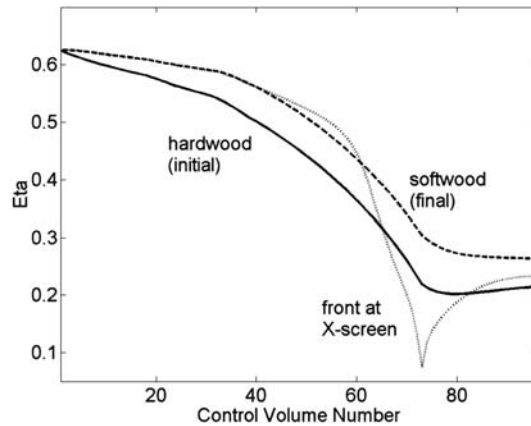


Figure 17.41. Compaction profile during MPC control of feedstock grade change from hardwood to softwood. The controller effects increase in temperatures and white liquor flow. This causes the digester to approach plugging-like conditions when the transition front approaches the extraction screen before stabilization at new steady-state conditions corresponding to softwood operation.

Table 17.7. Output/input pairings used for SISO loops.

		Case I		Case II		Case III	
		PI	MPC	PI	MPC	PI	MPC
IAE	Blow Kappa number	369	238	88	32	1921	247
	Residual EA	84	59	89	12	92	121
Settling Time (h)	Blow Kappa number	11.9	5.5	11.6	4.9	26.7	8.2
	Residual EA	7.2	1.9	11.2	—	9.7	8.7
	Residual EA						

(RTO). While there are degrees of freedom for optimization, there are constraints, which prescribe the feasible operating domain for the process.

RTO is normally applied to plant units, which are controlled effectively by appropriately designed control structures. For continuous processes, the focus has been on steady state optimization since the process stays at near steady state for a larger fraction of operating time. The need for dynamic optimization arises for continuous plants undergoing grade changes and for batch and semi-batch (fedbatch) processes.

Three broad categories of structures have evolved, depending upon the manner in which optimization is carried out. In the two-layer structure (Fig. 17.42a) which is normally applied for steady state optimization, a steady state optimizer sets the set point targets for the advanced controller. Since the steady optimizer is invoked only at the steady state condition, the optimizer is not active at all times. This deficiency is overcome in a three-layer structure where an intermediate optimization layer is introduced between the steady state optimizer and the advanced controller (Fig. 17.42a). The intermediate optimizer could be based on steady state LP, QP model or on a reduced order dynamic model and runs concurrently with the advanced controller. This structure has been widely applied in process industries. In a single layer structure, which has evolved recently, a dynamic real time optimizer sets the targets of the local controllers. In all the three structures, local regulatory controls are entrusted with the task of rejecting fast disturbance.

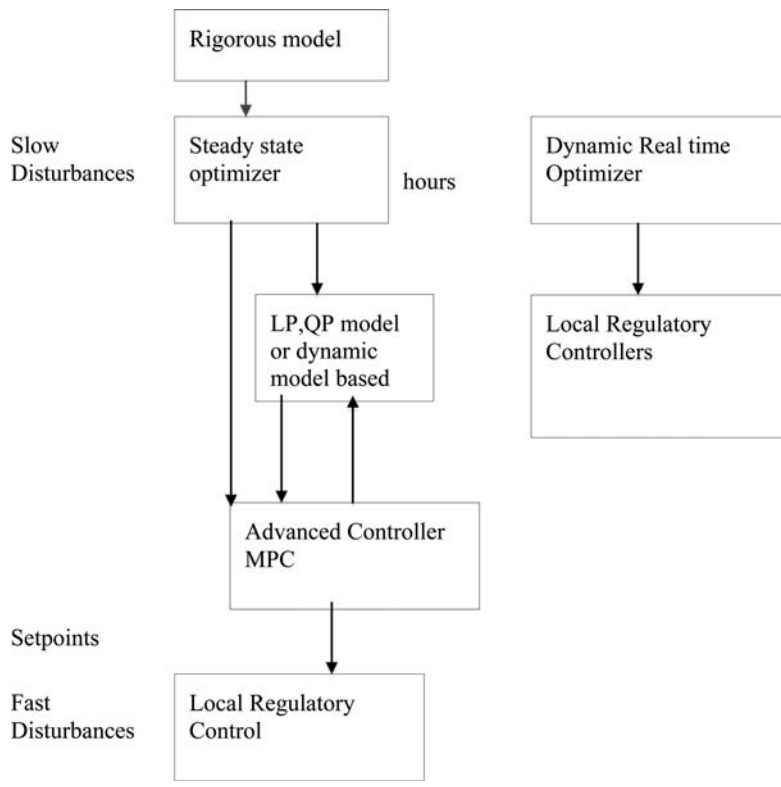


Figure 17.42. (a) Multilayer and (b) Single layer optimization frameworks.

Slower disturbances are handled in the higher-level optimizer. Model predictive controller (linear or nonlinear) is usually employed in the advanced control layer since it has the capability to accommodate a larger number of controlled variables. Optimization is required when disturbances affect the key variables requiring the plant to shift to a new optimal point. If the disturbances occur within the bandwidth of the process, then regulatory controllers are used to counter the effect of the disturbances. Optimization comes into focus when slower disturbances, which have a strong impact on the performance of the process, occur. If these disturbances occur frequently, then real time optimization becomes relevant. An example of the application of the two-layer structure has been in optimization of the biotechnological process of acrylic acid synthesis (Lunelli *et al.*, 2008).

Plant-wide real time optimization: For implementation of plant-wide RTO, three options are considered namely decentralized, decentralized with co-ordination, and centralized. Decentralized structures may yield sub-optimal results while centralized structure has to contend with a large-scale optimization problem. Decentralized structure with co-ordination is proposed as a viable alternative. The conceptual structure shown in Figure 17.43 has been proposed by Cheng *et al.* (2007) for plant-wide control of a paper pulp process. The coordinator use a plant level model to develop price co-ordination vectors for use in the optimization levels of each MPC. For the paper pulp process, four MPC controllers are used to cover digester and oxygen reactor, bleaching plant, recovery multiple effect boilers and lime/recausticizing sections.

Instead of the coordination approach, the one-layer direct optimization approach for plant-wide optimizing control of a bioethanol production process has been proposed by Ochoa *et al.* (2010). Central to the feasibility of this approach has been the use of an efficient optimization approach for solving the large-scale dynamic optimization problem.

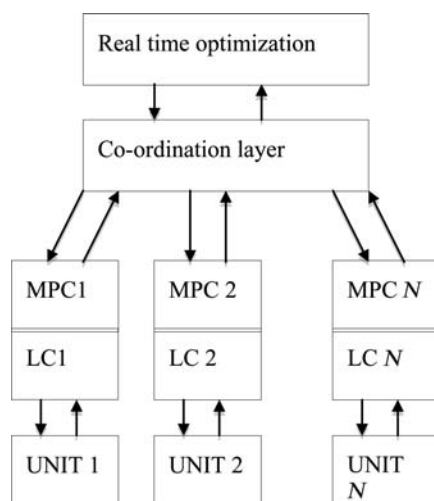


Figure 17.43. Co-ordination of real-time optimizer with MPC.

Dynamic optimization: Since batch and fedbatch fermenters operate under unsteady state conditions, dynamic optimization is invoked to ensure maximum productivity. Rigorous optimal control theory based on Pontryagin's maximum principle is used to develop these control profiles. In many of the fedbatch optimization problems, the feed rate policy could be bang–bang (switching between minimum and maximum limits) or a continuous singular profile (Modak and Lin, 1992). A different approach consists of solving the dynamic optimization problem as a nonlinear programming problem (see for example, Padhiyar *et al.*, 2006b). Bapat *et al.* (2006) used such an approach to determine the optimal feeding recipes for production of an antibiotic in a fedbatch fermenter. The model discussed in section 17.2.1.2 was used by Padhiyar and Bhartiya (2008) to determine optimal grade transition policies. The main difficulties in implementation of these optimal strategies are the open-loop nature of the strategies, lack of complete knowledge of the process model and non-availability of real time measurements of key variables. For a number of fedbatch fermentation problems, using singular extremes, it has been possible to develop state feedback formulation of the optimal control problem (Dewasme *et al.*, 2011). This leads to control structures, which are less sensitive to model parameter uncertainty. State feedback optimal control has been developed for a number of bioconversion processes like baker's yeast fermentation (Palanki *et al.*, 1990), ethanol production, and fedbatch fermenters. In some cases, heuristic control strategies (Smets *et al.*, 2004) which can be implemented with imprecise knowledge of the process model have also been proposed. However, this implementation requires reliable sensors for biomass concentration and an observer for specific growth rate. The implementation of dynamic optimizing control can also be realized with a two-layer structure (Fig. 17.42b). Dynamic optimizer prescribes set point trajectories to the lower level controller. Because of the nonlinearities involved, the lower level controller can be a nonlinear controller. The model reference controller structure proposed by Bhat *et al.* (1991) for control of fermenters could be a viable structure for the lower level controller.

17.9 CONCLUDING REMARKS

The case study problem represents in a broader sense complexities and challenges that would arise and that could arise in the control of biomass conversion processes. The control system designer has at his/her disposal a wide array of control strategies, which could be tailored suitably

to suit the specific static and dynamic character of the process in question. In fact, the synthesis of control structure for a total plant will involve a judicious decomposition of the overall control problem into a smaller set of control problems for which control strategies presented in this chapter could be used. In the literature, several systematic approaches have been proposed for control system synthesis. In the same vein, while optimization is used implicitly in the control calculations in controllers like MPC, its application to the total plant may require decomposition of the overall optimization problem into a smaller set of problems with a strategy of co-ordination of the operation of individual optimizers so that the desired plant optimum is reached. Models remain key to the design of control structures best suited to a specific process situation. With a well-chosen structure, which takes into account the process dynamics, and disturbance patterns affecting the process, the need for extensive field tuning exercises on the field can be reduced. With adaptation features incorporated in the structure as a credible approach to tackling process variability on-line, one has in place a monitoring mechanism, which can tackle departures of the control performance from the desired value and sensitize the controller to re-align it to recover from inferior performance levels to the best achievable performance levels.

17.10 QUESTIONS FOR DISCUSSION

- Discuss the difference between multivariable control *versus* just controlling single loops.
- What are the respective advantages and disadvantages for the two approaches?
- What are the respective advantages and disadvantages with rigorous models compared to simple models when they should use for control?
- Discuss the need for long-term maintenance of rigorous *versus* simple models?
- How will measurement faults affect the control accuracy? Discuss different types of measurement faults and different types of control.

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