Biomass Gasification

Chemistry, Processes and Applications

Jean-Pierre Badeau
Albrecht Levi
Editors

NOVA

Renewable Energy: Research, Development and Policies Series

BIOMASS GASIFICATION: CHEMISTRY, PROCESSES AND APPLICATIONS

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JEAN-PIERRE BADEAU
AND
ALBRECHT LEVI
EDITORS

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PREFACE

Biomass gasification means incomplete combustion of biomass resulting in the production of combustible gases consisting of carbon monoxide, hydrogen and methane. Amongst the renewable energies, the biomass is the most important energy source. Three types of biomass are available, one generated during the processing of wood in timber mills, another is energy plantation and third bio-residues generated during the processing of agricultural produce. Due to a booming population and increasing needs in life quality all over the world, energy demand is undergoing a great increase. To find alternative fuels and to increase the contribution of renewable energy to worldwide energy production, biomass wastes must be used for energy production. This book examines the importance of biomass gasification and assesses the possibility of biomass exploitation as an alternative to conventional fuel.

Chapter 1 - Biomass is a unique renewable energy fuel in that unlike other renewables, it is naturally available as a solid fuel, but can be converted into liquid or gaseous fuels. The world in 2005 used around 48 EJ of biomass energy, nearly all of which was combusted at low thermal efficiency as fuelwood in developing countries. Around 4.6 EJ was used in modern biomass systems, either as liquid transport fuels or as a solid fuel for boilers in power stations or heating units. At present, very little is gasified. The future use of gasified biomass will increasingly depend on its ability to deliver higher greenhouse gas savings at lower costs than other ways of using bioenergy. Because of the high efficiencies possible for combined cycle gas turbines, the potential for gasification is considerable, but cost reductions and further technical progress are still needed. Its potential could be enhanced if gasification combined with carbon capture becomes feasible.

Chapter 2 - In the near future, energy demand will have a great increase, due to the enhancing needs in life quality all over the world and especially from large emerging economies of Asian countries like India and China. Consequently, and as it has already happened in 2008, fuel prices may rise to levels that may threaten world economy, as we know it. Therefore, it is of most importance to find alternative fuels and to increase the contribution of renewable energy to worldwide energy production. These goals could be achieved by using biomass wastes for energy production, which would also allow decreasing large amounts of wastes with negative impact on environment and at he same time, decreasing CO_2 emissions and global warming. Thermochemical processes, like gasification applied to biomass wastes could be an alternative source of fuels and raw materials for several industries, as it allows the conversion of these residues into economical valuable

products, which can be used in broad applications. Another advantage of gasification is that it allows CO_2 separation for its sequestration.

As gasification gas is most dependent on biomass wastes characteristics, it is very important to full analyze the wastes to be processed, in order to characterize and classify the biomass wastes suitable to be treated by gasification. When wastes with considerable amounts of S, Cl and N are gasified, several undesirable compounds may be released into the gas phase, which may compromise gasification gas end-uses. Co-gasification of different types of biomass and other wastes may dilute the undesirable elements or compounds of some feedstocks, thus reducing the production of pollutants emissions that could result from the gasification of a single fuel. By the right manipulation of feedstocks blends it is also possible to improve gas quality and achieve the suitable gas composition for a certain gas end-use.

The success of biomass wastes gasification depends on the development of gas cleaning technologies. This chapter will analyze several gasification gas treatments, either thermal or catalytic to accomplish a considerable decrease of undesirable compounds to guarantee the production of a clean gasification gas with a wide range of applications. New and more efficient biomass gasification technologies will also be analyzed, like Integrated Gasification Combined Cycle (IGCC). The stages of deployment of new biomass wastes gasification will also be analyzed, enlightening the progresses already accomplished and the needs for further R&D (research and development).

Chapter 3 - Willow biomass is found to be an excellent fuel for farm-based power generation by utilizing an advanced gasifier system that uses high-temperature preheated air as the gasification medium. The gasifier's product fuel gas can be used in microturbines to generate electricity or used for other farm energy needs. The gasifier performance under various operating conditions is estimated using a previously developed gasifier model. The net gasification efficiency is about 85 percent under nominal operating conditions. The capital cost of a small, farm-based power system is estimated to be about $2,800/kW. Using the latest published information on willow biomass production cost, the cost of electricity is estimated to be 9 cents/kWh and is reduced to 7.2 cents/kWh when willow is grown on Conservation Reserve land. The costs associated with harvesting, handling, and transporting the willow biomass account for 40 to 50 percent of the annual operating cost. Results also show that co-gasification of willow with low-cost wastes, such as dairy farm animal wastes, can reduce fuel cost, increase the overall fuel availability and help work around problems resulting from seasonal availability of biomass crops. Co-gasification of willow biomass with manure waste also benefits the dairy industry by providing an economical way to dispose of farm wastes and manage nutrient flows.

Chapter 4 - Nowadays, biomass has a well-known potential for producing energy carriers, such as electricity, heat (steam) and transport biofuels. However, biomass availability is rather limited and stochastically distributed. This could be a major problem in demographically dense regions where land is scarce and biomass may compete with other applications, notably agriculture for food production. In fact, this is the case for the first-generation biofuels (e.g. bioethanol and biodiesel) that are mainly produced from biochemical conversion of food crops such as sugar cane, corn or wheat, and vegetable oils from feedstock like rapeseed or palm oil. Moreover, when taking into account emissions from transport and conversion treatments, life-cycle analyses reveal that first-generation biofuels frequently exceed the emission thresholds of fossil fuels.

Second generation biofuels are now being developed as a possible better alternative to the first generation, as they can use non-food crops (e.g. switch grass) or biowastes from different origins (e.g., forest, agriculture, industry, municipalities). Second generation biofuels can also be produced via either biochemical or thermochemical conversion. Among all the existing thermochemical conversion technologies, gasification is gaining interest due to its higher efficiency, larger scales, and reliable operation.

However, biowastes-to-biofuels conversion involves several challenges. Firstly, the existing technology must be re-designed and optimized to become cost and efficiency competitive with fossil fuels. Moreover, due to the wide diversity of biowastes and biofuels that can be obtained, the most sustainable conversion routes must be properly selected. Hence, an inherent challenge is to develop a reliable model to evaluate the sustainability of any process.

In this chapter the authors present the evaluation of second generation biofuels (SNG, methanol, Fischer-Tropsch fuels, hydrogen) as well as heat and electricity, from different biowastes via gasification with subsequent catalytic conversion of syngas. Pre-treatment steps are also considered in order to enhance the low energy density of biomass prior to gasification. However, since pre-treatment is directly affected by local conditions, the Dutch province of Friesland is taken as a case study. The biowaste-to-biofuels routes are modeled in Aspen Plus, and mass and energy balances obtained from simulations are later used for efficiency evaluation. Results are presented in terms of mass conversion yield, energy and exergetic efficiency. The last part of the paper is devoted to explain how those results will be integrated for combined economic and environmental impact analysis.

Chapter 5 - Amongst the renewable energies, the biomass is the most important energy source. Because of its wide spread availability, renewable in nature and potential in neutral in relation to global warming, the potential of biomass to help to meet the world energy demand has been widely recognized. Three types of biomass are available, one generated during the processing of wood in timber mills another is energy plantation and third bio-residues generated during processing of agricultural produce. Among these, bio-residues are available in plenty and their disposal in a benign way always poses a problem. Combustion, Gasification and Biomethaisation are the process of extracting energy from the biomass. For power generation, gasification is found to be economically viable at all capacities. Gasification is a thermo chemical process of converting the solid combustible in the biomass using substiochiometric quantity of air above 900˚C.

The composition of biomass indicates that C, H and O contents are more or less same in all biomass. Bio-Oxygen available in every biomass is sufficient to convert the solid combustibles into a gaseous fuel. The composition of the producer gas is found to vary from biomass to biomass. This is attributed to the ash content in each biomass and its composition. Ash catalyses the reaction and brings down the gasification temperature below 600˚C. This paves way for auto-gasification of biomass namely thermo-chemical conversion of solid combustible in biomass into gaseous fuel using bio-oxygen and catalytic ash. The feasibility of auto-gasification of various bio-residues and wooden logs has been established. Kinetics and Mechanism of auto-gasification has been elucidated using Thermogravimetric Analysis (TGA) data obtained with static air or nitrogen. In bio-residues such as rice husks, bagasse, coir pith, poultry litter etc., the temperature is uniform due to high porosity and the gasification takes place continuously. In wooden logs the temperature is not uniform. Therefore drying, devolatization and gasification take place simultaneously.

Chapter 6 - Biomass has lately experienced appreciable attention as a potential substitute for fossil fuels in electric power production. Renewable biomass crops, industrial wood residues, and municipal wastes as fuels for production of electricity provide substantial reduction of environmental impact. High reactivity of biomass makes it comparatively easy to convert solid feedstock into gaseous fuel for subsequent use in a power generating system.

The gasification of biomass is a thermal treatment, which ensues in a high production of gaseous products and small amounts of char and ash. Steam reforming of hydrocarbons, partial oxidation of heavy oil residues, selected steam reforming of aromatic compounds, and gasification of coals and solid wastes to yield a mixture of H_2 and CO, accompanied by water-gas shift conversion to produce H_2 and CO_2, are well-proved processes. Biomass gasification derived gas is a renewable fuel, which can be used for fuel cell applications.

Fuel cells and microturbines are electricity producers that undertake relevant energetic and environmental performances. They feature high electricity to input chemical energy ratios and availableness of high temperature heat.

The positive properties of fuel cells and microturbines for high efficiency power generation at any scale and of biomass as a renewable energy source which is not intermittent, location-dependent or very unmanageable to store, indicate that a combined heat and power system consisting of a fuel cell integrated with a wood gasifier may provide a combination for delivering heat and electricity cleanly and efficiently. Integration of both technologies has been under probe for quite long time.

Fuel cell technology is one of the most interesting energy conversion systems offering nearly zero emissions, flexibility of operation and high conversion efficiency. Increasing demand for power and the depletion of fossil fuels are offering opportunities for the development of fuel cells as power generating systems. The aim of this chapter is to assess the possibility of biomass exploitation for electric energy production in a given area.

Chapter 7 - In recent years, allothermal gasification has been receiving increased attention and a number of systems exploiting its advantages have been proposed or are under development. Allothermal gasifiers can offer a number of significant advantages over their more wide-spread counterparts, the autothermal gasifiers, especially for biomass gasification.

The main drawback of autothermal gasification, which generates heat in-situ by partial combustion of its feedstock, is the dilution of the product gas by products of combustion and inert gases (e.g., N_2) introduced in the oxidizer stream (e.g., air). As a result, air gasification yields a product gas with only low calorific value. To obtain high calorific product gas, pure oxygen is often used in autothermal gasification instead of air, as the oxidizer. This however, requires installation of air separation units, which results in higher construction and operation costs, plus efficiency penalty. Allothermal gasification, on the other hand, relies on the use of external heat sources to drive the endothermic gasification reactions within the gasifier. This physical separation of heat generation and gasification brings about the main benefits of allothermal gasification, i.e., absence of diluting gases from partial combustion of fuel feedstock within the gasifier and subsequent higher calorific value of the product gas.

However, the reliance of allothermal gasification on external heat supply also presents one of its main challenges, i.e., the effective transfer of heat between the heat source and the gasification chamber. Some systems use solid heat carriers circulating between two separate reactors while other systems rely on heat exchangers (e.g., heat pipes). The most suitable way for a particular gasifier configuration depends on both the heat source and the gasifier type.

The main aim of this chapter is to present a comprehensive overview of the state of the art in the field of allothermal biomass gasification. This chapter will introduce the field of allothermal gasification by presenting the different forms it can take, their main features and advantages. It will review recent developments in the area and highlight its successes.

Chapter 8 - Fixed-bed gasifiers are comparatively cheap to operate as they do not require the high pressures and small particle sizes required by fluidised bed gasifiers. There is a wide variety of biomass feedstocks that can be used in a fixed-bed gasifier. Wood is a common feedstock, but bark and other agricultural residues have also been used.

In fixed-bed gasifiers the different reaction stages (pyrolysis, combustion and reduction) occur within specific regions of the gasifier. This means that the different regions of the gasifier (e.g. the gas-char reduction zone) can be modelled separately.

Numerous models have been developed to simulate the processes occurring within fixed-bed gasifiers. The assumptions made and the processes simulated vary depending upon the available input data, operating conditions of the gasifier and the purpose of the model. In this review we examine the different strategies that have been used to model fixed-bed gasifier performance.

Chapter 9 - Currently, biomass gasification is considered as one of the most promising thermochemical technologies converting biomass into gaseous media for the production of power or fuels. The technical feasibility of producing fuels from biomass gasification is mainly affected by the contaminants present in the gasifier product gas (H_2S, tars, fly-ash, alkali and heavy metals, ammonia etc.), that act as poison for the catalysts used in the downstream upgrading units (Steam Reforming and Water Gas Shift). A commercial-like catalyst, containing 15.3 wt.% of Ni on $MgAl_2O_4$, and a home-made catalyst, containing 4.5 wt.% of Pt and Rh (4:1 as atomic ratio) on similar support, have been exposed to the product gas of a bench-scale downdraft gasifier having output of 10 kW_{th} and fed with wood pellets and using air like gasifying agent. Untreated and exposed catalysts were deeply characterized and the extent of deactivation was examined in the model reaction of steam reforming of methane. The exposure for 52 h to the biomass-generated gas mainly affected the metal dispersion and carbon deposition, but the catalysts still achieved very good performances. The Pt/Rh system showed a lower activity than that of the Ni catalyst, but sintering and carbon formation were less pronounced.

Chapter 10 - During biomass gasification process, high temperatures, high-pressure steam and sulfur containing compounds creates a severe environment for catalysts, so several attempts have been made to enhance the performance, and lots of kinds of catalysts were developed and applied. Among these catalysts, there was one kind of special catalyst with reactive oxygen species (ROS) - “mobile oxygen” in the catalysts structure. Based on the research results, these “mobile oxygen” catalysts exhibited superior resistance to carbon poisoned and/or sulfur-tolerant comparison to commercial catalyst because of these ROS. In this chapter, three kinds of the style catalysts will be illustrated respectively. Firstly, oxygen species such as dioxygen, atom adsorption oxygen and so on, relation and characteristic of these species was introduced. Then, metal “mobile oxygen” catalyst, such as Fe, Ce, Gd et al. was illustrated, the promotion by addition of these kinds of metal was introduced. Perovskite was another popular “mobile oxygen” catalyst was also mentioned. Lastly, our research on this kind of catalyst (mayenite, mayenite supported catalysts) was explained in detail.

Chapter 11 - High density plantations of fast-growing tree species grown on fertile land are today a viable alternative for the production of bio-fuels in many countries of cool-

temperate regions. For example in Sweden, willow biomass plantations are commercially grown for energy purpose. Rapid development of sustainable production systems and infrastructure, along with recent progress in tree crop breeding resulted in high biomass production potential on fertile agricultural land. In addition, tree plantations can increase biodiversity in open agricultural landscapes and serve as tools for the amelioration of environmental problems at local (e.g., waste product contamination through phytoremediation) and global scale (e.g. increased greenhouse effect through carbon sequestration). Thus, multifunctional biomass plantations offer additional possibilities in terms of, e.g., wastewater cleaning and carbon sequestration. However, the establishment and large-scale implementation of woody biomass plantations is often controversial due to, for example, presumed negative influences on biodiversity and the cultural heritage landscape, along with negative public attitudes. Conflicting interests of different parts of society and socio-political issues (e.g. agricultural and energy policy, market developments, public attitudes) are therefore major barriers for the rapid development of woody bio-fuel plantations in Sweden and many other countries, rather than climatic, technical or environmental constraints. In future, careful analysis of the non-technical, non-climatic barriers at regional level and possibly the development of guidelines for the establishment and sustainable, environmentally friendly management of woody biomass plantations could be means to boost the utilization of woody biomass from agricultural land in many countries of the world.

Chapter 12 - Biomass gasification technology emerged during the industrial revolution was successfully used in automobiles, public place lighting, urban household cooking and power generation during the second world war mainly in European countries. The developing countries richer in biomass resources and caught in the rising prices of fossil fuels have again shown interest in biomass technology. India being single largest user of biomass resources finds application in cooking and other house hold purposes. It may be noted that the conversion efficiency with biomass is very low (10 %) as against 80 % in boilers. Biomass combustion in traditional devices produces smoke, carbon monoxide and other health-damaging emissions. Therefore gasification technology requires using biomass resources more efficiently and in a cleaner manner. Judicious use of biomass gasification technology results in savings in fuel wood, furnace oil, diesel, LPG with implications of increased energy security.

Few attempts have been made to popularize biomass gasifiers on a commercial scale. The main reason is the wide spread availability of petroleum based fuels at low prices. Gasifier systems for hot water in hotels, midday meals, cremation, drying rubber, sericulture, tobacco curing are some of the applications wherein biomass technology comes handy. India being predominantly agricultural country requires major attention for the fulfillment of energy demands of a farmer. The increased use of diesel in agriculture and transportation sectors has resulted in diesel crisis. Finding an alternative fuel for diesel fuel is critically important for our nation’s economy and security. Producer gas from different biomass resources can act as a promising alternative fuel, especially for diesel engines by substituting considerable amount of diesel oil. Use of wood gasifiers to drive engines in single fuel mode of operation has the advantage of having complete independence from petroleum fuels. This feature is very convenient for electricity generation in more remote areas or areas inaccessible for long periods over the year. Further, compared to gasoline engines exhaust emissions like nitrogen oxides (NOx) and (hydro carbon) HC are lesser for producer gas operated gas engines. From derating and fuel flexibility point of view, dual fuel engines are highly acceptable.

Modification of existing diesel engine for dual fuel operation with producer gas is simple and power derating is limited to 20–30%. Diesel savings up to 70–90% have been reported for dual fuelling. The lower running cost and the use of alternative fuel sources with dual fuel engine operation has attracted many investigators to apply this type of engine in different areas. The main aspiration from the usage of dual fuel engine is mainly to reduce particulate emissions and nitrogen oxides. It is difficult to simultaneously reduce NOx and smoke in normal diesel engines due to the trade-off curve between NOx and smoke. One prospective method to solve this problem is to use oxygenated alternative fuels to provide more oxygen during combustion.

The present work is an effort to evaluate feasibility of popular alternative fuels in the form of non edible oils of Honge, Rice bran and Neem that are locally available and producer gas as a total replacement for fossil fuels. Experiments have been conducted on a single cylinder four-stroke compression ignition (CI) engine operated on single and dual fuel modes at injection timings of 19, 23 and 27^0 BTDC respectively and injection pressures varied from 205 and 280 bar. Earlier, in single fuel mode of operation, optimum conditions in terms of injection timings and injection pressures for Honge, Rice bran and Neem oils were determined.

Brake thermal efficiency in dual fuel mode of operation is lesser than single fuel mode of operation at all the injection timings investigated. However, it improved marginally when the injection timing was advanced for all the non edible oils tested. The smoke emission for producer gas–non edible oil combinations was found to be more than producer gas–diesel oil. The higher viscosity of non edible oils resulted in poor atomization and mixture preparation with air resulting in higher smoke. With dual fuel operation, smoke and NOx emissions were considerably reduced with increase in (corbon monoxide) CO emissions.

Chapter 13 - Bio-energy accounts for about 14% of the global primary energy supply. Biomass is mostly being used in an inefficient manner in the rural areas of developing countries that leads to a host of adverse implications on human health, environment, and social well being. Therefore, the utilization of biomass in a clean and efficient manner to deliver modern energy services to the world's poor remains an imperative for the development community. One possible approach to do this is through the use of biomass gasifiers. Considerable efforts have been directed towards developing and deploying biomass gasifiers in many countries however, scaling up their dissemination remains an elusive goal.

So far, the cumulative capacity of biomass gasification projects in India is far below their theoretical potential despite government subsidy programmes. One of the major barriers is the high costs of investments in these systems. The Clean Development Mechanism (CDM) of the Kyoto Protocol (KP) provides Annex-I (industrialized) countries with an incentive to invest in emission reduction projects in non-Annex-I (developing) countries to achieve a reduction in CO_2 emissions at lowest cost that also promotes sustainable development in the host country. Biomass gasification projects could be of interest under the CDM because they directly displace greenhouse gas (GHG) emissions while contributing to sustainable rural development. However, there are only two biomass gasifier project registered under the CDM so far. In this chapter, an attempt has been made to assess the CO_2 mitigation potential of biomass gasifier based projects under CDM in India.

The results indicate that in India around 74 million tonne agricultural residues as a biomass feedstock can be used for energy applications on an annual basis. In terms of the plant capacity the potential of biomass gasification projects could reach 31 GW that can

generate more than 67 TWh electricity annually. The annual CER potential of biomass gasification projects in India could theoretically reach 58 million tonnes. Under more realistic assumptions about diffusion of biomass gasification projects based on past experiences with the government-run programmes, annual CER volumes by 2012 could reach 0.4 to 1.0 million and 1.0 to 3.0 million by 2020. The projections based on the past diffusion trend indicate that in India, even with highly favorable assumptions, the dissemination of biomass gasification projects is not likely to reach its maximum estimated potential in another 50 years. CDM could help to achieve the maximum utilization potential more rapidly as compared to the current diffusion trend if supportive policies are introduced.

Chapter 14 - In china, considerable research has been carried out to develop advanced biomass technology in order to improve the biomass energy utilization efficiency. In this chapter, some recent research on biomass gasification technology is reviewed including down-draft gasifier, circulating fluidized-bed (cfb) gasifier, and biomass gasification for power generation (bgpg), and arc plasma gasifier. The project background, technology adopted, current status, process economics and existing problems of the following two demonstration projects are discussed in detail: (1) the integrated biomass gasification and gas-supply system demonstration project in shandong province: demonstration stations for biomass gasification and gas-supply were constructed in rural villages in this project. These stations processed agricultural residues such as straw into gas fuel using down-draft gasifiers. (2) the biomass gasification and power generation system demonstration project in hainan province: an mw-scale biomass power plant was constructed at the sanya timber factory. This biomass power plant adopted advanced cfb gasifier system, and made use of the wood waste generated in the sanya timber factory as fuel, and reached the electricity generation capacity up to 1.2mw.

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Chapter 1

A GLOBAL PERSPECTIVE ON BIOMASS GASIFICATION

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ABSTRACT

Biomass is a unique renewable energy fuel in that unlike other renewables, it is naturally available as a solid fuel, but can be converted into liquid or gaseous fuels. The world in 2005 used around 48 EJ of biomass energy, nearly all of which was combusted at low thermal efficiency as fuelwood in developing countries. Around 4.6 EJ was used in modern biomass systems, either as liquid transport fuels or as a solid fuel for boilers in power stations or heating units. At present, very little is gasified. The future use of gasified biomass will increasingly depend on its ability to deliver higher greenhouse gas savings at lower costs than other ways of using bioenergy. Because of the high efficiencies possible for combined cycle gas turbines, the potential for gasification is considerable, but cost reductions and further technical progress are still needed. Its potential could be enhanced if gasification combined with carbon capture becomes feasible.

INTRODUCTION: PRESENT AND FUTURE FOR BIOMASS FUELS

Biomass is unique among renewable energy sources in that it is naturally available as a solid fuel, but can be converted into liquid or gaseous fuels. In 2005, the world consumed a total of about 493 EJ of primary energy (EJ =exajoule=10^{18} joule). Of this about 48 EJ, or 10 %, was biomass, mostly in the form of fuelwood burned at low thermal efficiency in developing countries [International Energy Agency (IEA) 2007a,b], with only about 4.6 EJ used as modern biomass. In 2006, 50 billion litres of ethanol was produced, mainly in the US and Brazil, along with about 5.4 billion litres of biodiesel, mainly in Europe, for a total of 1.4

EJ [Renewable Fuels Association 2008]. Another 3.2 EJ was used as a solid fuel in power stations and boilers [IEA 2007a], particularly in northern Europe, where it is an important fuel for combined heat and power systems (CHP).

At present, nearly all liquid fuel crops are produced from food crops—mainly corn in the US, sugar cane in Brazil, and oil seeds in Europe. Thus the prospects for further growth in liquid fuels from foodstuffs—whose starches are readily converted into ethanol—appear limited [Moriarty and Honnery 2008]. On the other hand, only cellulosic feedstock is used as a fuel in boilers, whether for heat or electricity.

CHP schemes make sense in cold climates, particularly if building and population densities are high. Faaij [2006] reports that such schemes, if in the 1-10 MW electric capacity range, can attain total efficiencies of 80-100 %. CHP schemes would be less easy to implement in the lower density cities of US or Australia. Further, in many parts of both countries, space heating is only needed for a few months per year, if at all. For example, the average annual (24 hour) temperatures in Stockholm and Helsinki (capital cities of the two leading biomass-using nations, Sweden and Finland) both at around 60 ºN, are 5.8 and 4.5 ºC respectively. In contrast, average temperatures in Sydney, Australia (30 ºS), and Los Angeles (30 ºN) are 16.8 and 16.5 ºC respectively [WorldClimate 2008].

How important could bioenergy be in future? Published estimates for biomass supply potential in the year 2050 vary very widely. Fischer and Schrattenholzer [2001] estimate a total of 370-450 EJ, with 221-244 EJ coming from forest, farm and municipal wastes, and the rest from energy plantations. The Intergovernmental Panel on Climate Change give a greater range, 125-760 EJ, mostly from energy plantations [Barker et al. 2007]. The greatest range is that of Hoojwijk et al. [2003], who estimate that biomass potential in 2050 will be 38-1174 EJ, with nearly all (8-1098 EJ) derived from energy plantations, and only a modest contribution (30-76 EJ) from wastes. Rhodes and Keith [2008] also stress the wide variation in estimates, and while sceptical of the higher values, argue that deep uncertainties will remain, in part because of the ethical questions involved. A recent World Bank study, for example, claims that 75 % of recent global food price rises can be attributed to the growth in biofuels from foodstuffs [Ngo 2008]. The future of cellulosic biofuel plantations are also in doubt because of concerns about how ‘green’ such biofuels really are [Moriarty and Honnery 2007a, 2008, Scharlemann and Laurance 2008].

What is reasonably certain is that modern uses of biomass will be far greater than their present low level of 4.6 EJ, and that cellulosic biomass will be the main feedstock. The important question then arises as to whether modern cellulosic biomass should be used directly as a solid, converted to a liquid such as ethanol, or gasified. Clearly, since the limits for total biomass potential also set the limits for biogasification potential, the large uncertainty apparent in overall biomass potential will also affect biogasification potential. Of course, the potential for biomass, and thus gasification, varies greatly from country to country.

THE PROSPECTS FOR BIOMASS GASIFICATION

Although many reasons have been advanced for encouraging biomass energy [Moriarty and Honnery 2007a], increasingly, the key argument for more use of modern biomass is that

it enables reductions in fossil fuel consumption, and thus reductions in greenhouse gas (GHG) emissions. Hefner [2002] sees the future as 'the age of energy gases' because of their convenience and efficiency of use, but this is not true for transport fuels. It is therefore necessary to compare the various options for biomass in terms not only of cost, but also on their relative GHG reductions from displacing fossil fuels. In some cases, the choice is simple: biomass gasification is the technology of choice for liquid biological wastes such as sewage and feedlot manure, and occurs naturally in landfilled organic garbage to produce landfill gas. Because of the anaerobic nature of decomposition, these sources have a high methane content. As an added benefit, use of such methane avoids release into the atmosphere, where it is an effective GHG [Cuellar and Webber 2008].

The short-term prospects for the various options need to be separated out from their long-term ones, as their rankings may change over time [Hamelinck and Faaij 2006]. Further, biomass in any form must be compared for cost effectiveness with all other approaches to mitigation, including other alternative fuels, carbon capture and sequestration (CCS), and energy conservation. The GHG benefits of biomass depend not only on whether it is used as a gas, liquid or solid, but also on the purposes for which it is used. The main possible uses are for liquid or gaseous direct transportation fuels, for electricity production, or for supplying heat to buildings or industry.

For transport, direct use of gas as a fuel does not give much efficiency gain over use of conventional liquid fuels [Hamelinck and Faaij 2006]. Unlike gases, however, alternative liquid fuels fit in well with existing land based transport systems [Honnery and Moriarty 2007]. For spark ignition engines, one alternative, methanol, can be produced from natural gas or from the sygnas produced from gasified biomass. Methanol, like biomass-derived ethanol, can easily blend with gasoline and if used in relatively small blend ratios requires little alteration to existing engines and fuel delivery systems. For diesel-fuelled vehicles, biomass gasification can lead to production of alternatives such as dimethyl ether and synthetic diesel via the Fischer-Tropsch process. At present, global production of these fuels is dominated by coal and natural gas feedstocks [Wang et al. 2008]. For many countries, large scale production of liquid fuels via gasification of biomass will ultimately depend on the relative costs of fossil fuel and biomass feedstocks, rather than potential GHG reductions, although these can be signficant. While increasing scarcity of conventional crude oil may see relative costs favour biomass in the short to medium term, lack of biomass availabilty at the scale necessary will place an upper limit on total supply, well below current fuel usage [Moriarty and Honnery 2007a]. One final option is production of hydrogen from biomass for use in hydrogen fuel cell vehicles. Apart from cost, limiting this at present are technical isses related to hydrogen purity and storage, and as Schafer et al. [2006] suggest, fuel cell vehicles are still a long way from mass production.

Using gases for electricity production, is, however, very efficient if combined cycle gas turbine technology (CCGT) is employed in large output plants. Further, gasified biomass can be co-fired with natural gas in existing gas turbines, and is thus a good fit with existing power generation. Although small-scale wood-burning Rankine cycle power plants have electrical efficiencies as low as 15-20 %, gasified biomass, if co-fired with natural gas in a large-output CCGT plant, can achieve overall efficiencies for electricity generation of over to 50 % [Faaij 2006, Walter and Llagostera 2007]. Combined cycle technology could get a boost from plans for carbon capture; one approach is to gasify the coal fuel into H_2 and CO_2, followed by separation of the CO_2. It is even possible that coal gasification could proceed in the absence

of carbon capture, given the energy efficiency advantages of combined-cycle gas turbines [Pearce 2008]. If so, gasified biomass could also be co-fired with gasified coal. Nevertheless, bio-gasification will find it difficult to compete in cold regions where CHP schemes can be implemented, given their already high overall efficiency and proven technology.

Rhodes and Keith [2005, 2008] have made a case for biomass gasification together with CCS, in effect giving negative emissions. At present, CCS is only suitable for large CO_2 sources such as fossil fuel power stations and cement plants, which together account for around a third of total energy-related CO_2 emissions [Pearce 2008]. Biogasification, if combined with CCS, promises an indirect way of capturing emissions from other fossil fuel systems, such as petroleum-fuelled transport, where capturing the CO_2 directly would be too expensive.

Co-firing with natural gas is only a medium-term solution. It appears quite likely that the global peak in natural gas production is only 1-2 decades away [Association for the Study of Peak Oil and Gas 2008], and will be increasingly unavailable for power generation. Even coal could peak in a similar time frame [Energy Watch Group, 2007]. Biomass gasification will then represent the only possible source of gas in the long-term. However, if large bio-gasification plants are built to take advantage of economies of scale, then a correspondingly large surrounding area is needed to grow the biomass, especially if it is on non-agricultural, marginal land, with low yields. Biomass transport costs are then high [Gagnon 2008]. True, biomass pellets can be imported, but biomass imports cannot be a general solution for the world. On the other hand, if small bio-gasification plants are built for electricity generation, the unit costs for the electricity will be high. Bridgwater [2007] has shown that for a variety of biomass to electricity systems, including CCGT, the unit costs are heavily dependent on capacity, particularly below 5 megawatt net output.

One additional advantage of electricity production via biomass gasification over coal, direct biomass firing and co-firing, is that exhaust emisisons of SOx, NOx, particulates and CO are likely to be lower [Overend, 2003]. Of all the technologies available, combined cycle natural gas shows the least emissions. Achieving low emission levels largely depends on the type of gas clean-up technology and gasification process used [Wang et al. 2008]. For all biomass systems, gas clean-up is likely to be essential if operating a CCS plant, which will add additional costs relative to natural gas systems. Clean-up costs could be expected to be minimised through use of biomass feedstocks from a standardised energy crop or residue. The presence of heavy metals in wood waste, for example, represents a considerable hazard. Apart from improving the exhaust emission profile of the plant, use of gas clean-up technology can also be expected to improve overall system efficiency through reduction and conversion of the char and tar produced [Wang et al. 2008].

DISCUSSION

Although biomass is by far the most commonly used form of renewable energy in the world, the proportion of modern biomass is small at around 10 % of all bioenergy, and is presently used either as a liquid for transportation or as a solid fuel for boilers. Food crops are presently used to produce transport fuels, as these are readily converted into liquids, but if biomass is to have any future, cellulosic biomass will have to be the dominant feedstock for

all uses. At present, the most cost-effective use of cellulosic biomass seems to be in CHP schemes, which can deliver high overall efficiencies. However, such schemes are not suitable for warmer climates.

Although there are great uncertainties in the future potential for biomass globally, there is little doubt that modern use of biomass will rise greatly. A large, efficient biogasification plant for electricity production, for example, might be sized at 100 MW net output. Its continuous operation would require about 0.01 EJ/year of biomass, which means that an increase of only 10 EJ in modern bioenergy use could support 1000 such plants. If in future gasification plants are not built in any numbers, it will not be due to lack of biomass resources. The limited availability of waste biomass will mean that very large-scale bioenergy production (hundreds of EJ) will be constrained by future demand for food and water, but even 30-50 EJ of modern biomass energy could support a large biogasification industry.

The future use of gasified biomass will increasingly depend on its ability to deliver higher GHG savings in a cost-effective manner, compared not only with other ways of using biomass, but also with other alternative fuels, and even with other methods of climate change mitigation. Because of the high efficiencies possible for combined cycle gas turbines, the potential for gasification is high, but cost reductions and further technical progress are still needed. However, CCGT technology also offers the possibility of low cost carbon capture and subsequent sequestration which could work in favour of biogasification in a carbon-constrained world.

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Chapter 2

INNOVATION ON BIOMASS WASTES UTILIZATION THROUGH GASIFICATION AND CO-GASIFICATION. STAGE OF DEPLOYMENT AND NEEDS FOR FURTHER R&D

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ABSTRACT

In the near future, energy demand will have a great increase, due to the enhancing needs in life quality all over the world and especially from large emerging economies of Asian countries like India and China. Consequently, and as it has already happened in 2008, fuel prices may rise to levels that may threaten world economy, as we know it. Therefore, it is of most importance to find alternative fuels and to increase the contribution of renewable energy to worldwide energy production. These goals could be achieved by using biomass wastes for energy production, which would also allow decreasing large amounts of wastes with negative impact on environment and at he same time, decreasing CO_2 emissions and global warming. Thermochemical processes, like gasification applied to biomass wastes could be an alternative source of fuels and raw materials for several industries, as it allows the conversion of these residues into economical valuable products, which can be used in broad applications. Another advantage of gasification is that it allows CO_2 separation for its sequestration.

As gasification gas is most dependent on biomass wastes characteristics, it is very important to full analyze the wastes to be processed, in order to characterize and classify the biomass wastes suitable to be treated by gasification. When wastes with considerable amounts of S, Cl and N are gasified, several undesirable compounds may be released into the gas phase, which may compromise gasification gas end-uses. Co-gasification of different types of biomass and other wastes may dilute the undesirable elements or compounds of some feedstocks, thus reducing the production of pollutants emissions that could result from the gasification of a single fuel. By the right manipulation of feedstocks

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blends it is also possible to improve gas quality and achieve the suitable gas composition for a certain gas end-use.

The success of biomass wastes gasification depends on the development of gas cleaning technologies. This chapter will analyze several gasification gas treatments, either thermal or catalytic to accomplish a considerable decrease of undesirable compounds to guarantee the production of a clean gasification gas with a wide range of applications. New and more efficient biomass gasification technologies will also be analyzed, like Integrated Gasification Combined Cycle (IGCC). The stages of deployment of new biomass wastes gasification will also be analyzed, enlightening the progresses already accomplished and the needs for further R&D (research and development).

Keywords: type of biomass wastes, catalytic gasification, hot syngas cleaning processes, syngas utilizations.

1. INTRODUCTION

There is a global effort to diminish greenhouse gas emissions through increasing the share of renewable fuels for energy production and to separate and sequester CO_2. European Union aims to increase the share of renewable energy sources from around 5.4% in 1995 to 12% of gross consumption by 2010, as declared in the White Paper for a Community Strategy and Action Plan - COM(97)599.

Due to the importance of biomass in many countries, there is a great interest in developing and commercializing innovative biomass energy conversion technologies. In the Biomass Action Plan - COM(2005)628 the European Commission recommended measures to increase biomass use from 69 Mtoe in 2003 to about 150 Mtoe in 2010. Biomass gasification may play an important role in achieving this goal, as the gases produced after cleaning procedures can substitute fossil fuels, in conventional and advanced energy conversion devices and can also be used as synthesis gas.

Different types of biomass or biomass wastes such as forest, agricultural and organic processing residues with moisture contents lower than 50% can be gasified with air, or oxygen and/or steam to produce syngas. Syngas may be used as a fuel or as a synthesis gas to produce liquid fuels, fertilizers and chemicals. Synthetic or substitute natural gas and hydrogen can be also obtained from syngas.

Biomass gasification has been extensively studied and different technologies have been developed. However, in Europe, the actual commercial uses are restricted to CHP and co-firing, both with large plants with about 15 MWth and small-scale plants with around 250 kWe (www.gastechnology.org/iea). A large number of biomass gasification plants are deployed in Asian countries, operating intermittently. Biomass gasification technologies are expected to play an important role in future energy systems, as they can decrease greenhouse gas emissions and the overall efficiency of these installation can be increased in combined cycles with gas and steam turbines and high-temperature fuel cells.

Biomass gasification can be very important in achieving the EU directives and North America decisions towards the reduction of greenhouse gases emissions and prevent global warming. Biomass growth in a sustainable basis absorbs most of CO_2 released during its

utilization. Besides, biomass use for energy production, through gasification also allows decreasing large amounts of wastes with negative impact on environment and reducing the dependency on imported fossil fuels, by producing alternative fuels.

However, biomass gasification integrated with gas cleaning technologies is still under development and further demonstration of these technologies is still needed. The technical, economical and environmental viability of these processes depend on achieving effective gas cleaning technologies that may decrease considerably the contents of tar and pollutant precursors like S, N and Cl compounds, especially important when biomass wastes with high contents of these elements are gasified. As these installations are expensive to build and operate, appropriate policies and significant incentives for market entry of these processes and products are required.

This chapter reviews biomass gasification processes that allow increasing gasification performance and gas quality and characteristics. Catalytic gasification and the main types of catalysts used during gasification and for fuel gas treating are reviewed and discussed. The main fuel gas cleaning processes are discussed according to fuel gas utilization.

Besides, the advances of biomass gasification, more efficient biomass gasification technologies like Integrated Gasification Combined Cycle (IGCC) are analyzed, as the great energy management of these installation allows high energy conversion efficiency. The needs for further research and developments are also enlightened, such as: development of low cost and more efficient catalysts for gas cleaning, new catalyst regeneration processes, new gas separation technologies, advanced gas turbines and fuel cells technologies. These developments will allow improving the technical, environmental and economical viability of biomass gasification.

2. BIOMASS GASIFICATION FUNDAMENTALS AND MAIN REACTIONS

Conventional termochemical processes achieve a high conversion of solid fuels into energy through combustion. Other processes include a partial conversion, as in the case of charcoal production from wood. All these processes use as a start material a solid fuel that will be involved in a complex reaction system of physicochemical transformations that are promoted by the effect of higher temperatures or the reaction of gaseous species present on the surrounding atmosphere. The possible reaction products may include a complex gaseous mixture, a solid residue or even a liquid phase. In some cases this reactions are exothermal, being possible to capture this energy as a valuable product. Gasification is the common designation of the processes where gaseous species are obtained from a solid fuel, through an assembly of chemical reactions and physical transformations (Souza-Santos, 2004).

In a more detailed way, the processes that occur during the heating of solid fuels are:

- *Drying*: this process occurs at temperatures until around 380 K (107ºC), there is mainly a release of water vapor from the surface and the inner pores of the solid fuel. Some of the more volatile organic and inorganic components of the fuel may also be released.
- *Devolatilization or pyrolysis*: by increasing temperature, a transformation of the structure of the solid fuel is promoted, originating new chemical species. These

processes originate three main products, specifically light gases, tar and char. The main components of the gaseous mixture are H_2, CO, CO_2, H_2O, CH_4 and other hydrocarbons. Other compounds like NH_3, H_2S or phenols may also be formed. Tar fraction includes heavier organic compounds that are gaseous when they are released during the pyrolysis or are dragged as liquid drops. Char is composed mainly from carbon and the mineral matter present on the solid fuel.

- *Gasification or combustion*: this process includes the main heterogeneous reactions between the solid fuel (or the char) and the chemical species present in the surrounding atmosphere. These gaseous species include those released during the drying and pyrolysis, but generally are externally supplied to the process. Combustion processes demand the use of oxygen (from atmospheric air or even pure) while other processes include the use of water vapor, hydrogen or other gases. A large number of homogeneous reactions occur also between all the species present on the gas phase, which result in a reduction of the amount of those that are more reactive or thermodynamically more unstable.

The main compounds that result from a combustion process are CO_2 e H_2O, whose amounts depend directly on the fuel composition. Gasification processes however, by the use of water vapor or oxygen as reactants, originate a more complex mixture, including CO, H_2, CO_2, CH_4 and H_2O, sometimes known as synthesis gas.

The gasifying agent can be air, oxygen, steam, carbon dioxide or a mixture of all or several of the mentioned components. Air or oxygen promotes biomass partial oxidation, supplies the heat necessary to the endothermic reactions and produces H_2O and CO_2 for further reduction reactions. Due to the high nitrogen contents of air, the heating value of the gasification gas is very low. The use of oxygen, instead of air, allows increasing the heating value of the fuel gas, but the operating costs of the process also increases due to the high cost of oxygen production. The use of steam is also beneficial, because it allow increasing both the hydrogen content of the fuel gas and also its heating value, which is about 10-15 MJ/Nm^3, against the 3-6 MJ/Nm^3 for biomass gasification with air, as reported by Wang et al., 2008. The presence of CO_2 in the gasifying agent has the advantage of converting char, tar and methane into H_2 and CO, especially in presence of Ni/Al catalysts, but requires an external heat supplier. Therefore, the effect of using mixtures of all these components has been studied.

The gasification gas, after cleaning, purification and drying may be used directly as a gaseous fuel or as feedstock for organic synthesis, using catalyzed techniques like the Fischer-Tropsch process or methanol synthesis. The obtained products, mainly liquids may either be used as fuels or in chemical industries.

When the temperature of the he char obtained after the previously presented phases reaches a certain degree, generally considered higher than 700ºC (973 K) occur a large number of reactions involving the solid carbon and the several components of the surrounding atmosphere. These reactions are presented in Table 1, including the respective enthalpies.

Combustion reactions between carbon and oxygen (1) and (2) are exothermal and as long as that they occur in sufficient scale, provide the required energy for the drying and pyrolysis phases of the fuel. The resulting products are carbon dioxide and monoxide, in different proportions, depending mainly of the temperature and the equivalent ratio (ER) of the process.

Table 1 Mechanisms e enthalpy of the gasification and combustion reactions. (Smoot, L.D. and Smith, P.J., 1985)

Designation	Mechanism	ΔH (kJ/mol)	
Oxidation	$C_{(s)} + O_2 \leftrightarrows CO_2$	-392,5	(1)
	$C_{(s)} + ½\ O_2 \leftrightarrows CO$	-110,5	(2)
Boudouard	$C_{(s)} + CO_2 \leftrightarrows 2\ CO$	172,0	(3)
Water Gas: primary	$C_{(s)} + H_2O \leftrightarrows CO + H_2$	131,4	(4)
secondary	$C_{(s)} + 2\ H_2O \leftrightarrows CO_2 + 2\ H_2$	90,4	(5)
Methanation	$C_{(s)} + 2\ H_2 \leftrightarrows CH_4$	-74,6†	(6)
Water-gas shift	$CO + H_2O \leftrightarrows CO_2 + H_2$	-41,0	(7)
Steam Reforming	$CH_4 + H_2O \leftrightarrows CO + 3\ H_2$	205,9†	(8)
	$CH_4 + 2\ H_2O \leftrightarrows CO_2 + 4\ H_2$	164,7†	(9)
	$C_nH_m + n\ H_2O \leftrightarrows n\ CO + (n + m/2)\ H_2$	210,1†‡	(10)
	$C_nH_m + n/2\ H_2O \leftrightarrows n/2\ CO + (m-n)\ H_2 + n/2\ CH_4$	4,2†‡	(11)
CO_2 Reforming	$CH_4 + CO_2 \leftrightarrows 2\ CO + 2\ H_2$	247,0†	(12)
	$C_nH_m + n\ CO_2 \leftrightarrows 2n\ CO + m/2\ H_2$	292,4†‡	(13)
	$C_nH_m + n/4\ CO_2 \leftrightarrows n/2\ CO + (m-3n/2)\ H_2 + (3n/4)\ CH_4$	45,3†‡	(14)
H_2 Reforming	$CO + 3\ H_2 \leftrightarrows CH_4 + H_2O$	-205,9†	(15)

Equivalent ratio is defined as the ratio between the oxygen supplied to the system and the oxygen stoichiometrically required for the total combustion of the fuel. ER values higher than 1 originate mainly carbon dioxide. On gasification processes ER values are much lower, originating higher fractions of carbon monoxide, depending on the temperature and the fuel used.

Solid carbon may react with carbon dioxide according to the Boudouard reaction (3) originating CO. This is an endothermic process that occurs mainly at temperatures higher than 1000 K and is inhibited by the presence of CO.

Water gas reactions, (4) and (5), involve solid carbon and water vapor, are endothermic and favored by higher temperatures and lower pressure.

Methanation or hydrogasification, reaction (6), occurs between carbon and hydrogen. It is generally very slow, but favored at higher pressure.

Increasing temperature may cause a displacement of the chemical equilibrium of the homogeneous "water gas shift reaction" (7), between CO, water vapor, hydrogen and CO_2. This reaction may have a very clear effect on the composition of the obtained gaseous mixture, changing the ratio CO/H_2.

Methane and all the other hydrocarbons present on the gas phase may suffer several reforming reactions, (8) to (14) with either water vapor or CO_2, increasing CO, H_2 or methane concentration. These reactions, being endothermic processes are the cause of the evolution of hydrocarbon concentrations that is observed at higher temperatures.

Hydrogen reforming (15) occurs between CO and hydrogen with the production of methane and water vapor. This reaction, while causing an increase of the gas heating value,

generally occurs at a low extent, except at higher pressure or under the effect of the appropriate catalysts.

Several other reactions occur also with major importance on the final gas composition. The most significant will be cracking reactions where thermal action causes a breakage of the heavier hydrocarbon molecules, with the formation of lower mass gaseous species.

There are different types of biomass gasifiers: fixed beds, moving beds, fluidized beds and entrained flows. Fixed beds and moving beds are simple and reliable reactors, but have low and non-uniform heat and mass transfer and thus produce high large amounts of char, tar and particulates. Fluidized beds require almost no biomass pre-treatment and they have uniform heat and mass transfer, due to the presence of hot inert bed materials, normally silica sand. Therefore, they have high and uniform heating rates and high productivities, hence, biomass is converted to syngas at around 800-900°C. Fluidized beds are easy to design and built and easy to operate and to temperature control. The technology developed for the production of heat and/or electricity has been demonstrated with biomass. Due to the lower temperatures, the gas produced contains tar and hydrocarbons and needs catalytic upgrading.

Entrained flow gasification needs fuels with very small fuel sizes and as most biomass feedstocks are not suitable to be directly introduced into an entrained flow gasifier, extensive pre-treatment is required. This process needs high temperature, around 1300°C, but it can be decreased to 1000-1100°C, when the biomass has catalytic active components like potassium or sodium, as it happens for straw and black liquor. Due to the higher gasification temperatures, the gas obtained has little or no hydrocarbons. The main disadvantage of this process is the need to grind biomass into small particles, however, this disadvantage may be overtaken by combining it with the following processes:

- Slow pyrolysis: biomass is pyrolysed at 500°C into a char, which is pulverised and introduced into the entrained flow gasifier. The Choren process (Germany) uses this approach and injects the char into the high temperature syngas to cool it by endothermic heterogeneous gasification reactions, which increases the efficiency of the process.
- Flash pyrolysis: biomass is also pyrolysed at 500°C into a slurry of liquid oil and char, which is injected into an entrained flow gasifier. FZK in Germany is developing this process in cooperation with Future Energy (www.gastechnology.org/iea).
- Torrefaction: biomass is treated at 250-300°C to produce a fragile and easy to pulverize fuel, which has a high energy density. Therefore, torrefaction may be done before biomass transporting, decreasing feedstock transport. ECN (Energy Research Centre of the Netherlands) has study this pre-treatment option (www.gastechnology.org/iea).
- Fluidized bed gasification: biomass is gasified at 600-900°C and a gas with small char particles is produced, which is introduced into the entrained flow gasifier to convert it to syngas.

Some of these options may not be competitive or even advantageous, depending on biomass type and availability and on syngas utilization.

3. Effect of Biomass Wastes Characteristics on Fuel Gas Composition

3.1. Effect on Hydrocarbons Content

The three main biomass components are cellulose, hemicellulose and lignin.

Cellulose is a natural, renewable organic compound and the most abundant on earth, with an average of 40 to 45% of most biomass sources. Structurally it is a linear polymer with more than 10 000 units of glucose or 1,-4-D-glucopyranose. As it possesses a large number of intra and intermolecular connections based on hydrogen bonds, this molecule is very stable, insoluble in most solvents and resistant to acid or enzymatic hydrolysis.

Hemicellulose is an irregular mixture of polysaccharides with glucosidal connections. Its base units are very diverse sugars including besides glucose, several hexoses (C_6 sugars) and pentoses (C_5 Sugars). It presents smaller polymeric chains than cellulose, between 100 to 200 units and is more soluble in alkaline solutions and more hydrolysable. Hemicellulose represents between 20 to 30% of the biomass of most plants.

Lignin amounts to around 25 to 35% of biomass material. It is a very long chain polymer with a large fraction of aromatic units and a strong network of C–C cross-linked connections that are responsible for its high mechanical strength. It is present in cell walls and is hydrophobic, in opposition with cellulose which is hydrophilic and more permeable to water conduction inside the plants. Lignin present a mass fraction of more than 60% of carbon and 30% of oxygen, which contrasts with the corresponding fractions of around 50% of carbon and 50% of oxygen presented by cellulose and hemicellulose.

Human civilizations have been using biomass on thermo-chemical processes since a very long time. Wood pyrolysis was probably one of earliest chemical process on ancient societies. Old Chinese civilizations used wood distillation, while Egyptians, Greeks and Romans have obtained charcoal from wood, while capturing the release volatiles for use on embalming and ship building (Goldstein I.S et al., 1981).

In 1760, in England, coke produced from charcoal was used for house heating, as it present a heating value 50% higher than dry wood. Charcoal was also used on meat packing, printing inks and several medical applications. Until 1800 wood carbonization was the most used pyrolysis process, to supply the large amounts of coke needed on steel production. After 1876 the main use of wood charcoal has been the steel and iron industry.

The expansion of chemical organic industry and paint industry increased the need for methanol production, being the favored method the collection of all the volatile fractions released during wood pyrolysis. Around 1900 destructive wood distillation was a large scale industrial process through heating wood in cast iron retorts. On the early years of the 20th century wood was the major source of methanol, acetic acid and acetone. Due to this extended use, charcoal became a major byproduct, available in large amounts and with low costs. This phase of large scale wood use was however relatively short, as the beginning of the oil industry caused the dismantling of the existing industrial facilities.

It was only on the second half of the 20th century and due to the oil crisis that wood (or biomass) was again considered as a viable method for the production of gaseous fuels or synthesis gas at large scale. Recent studies have begun to identify biomass gasification as a viable energy conversion process. While the available amounts of fossil fuels like oil or coal

are being depleted, studies on biomass has an energy source have increased over time, as part being among the sustainable and renewable sources of energy, besides solar, wind or hydropower.

Scientific studies on biomass gasification have focused on the optimization of the different process parameters that affect gas production. Generally this process is conditioned by external variables like temperature, pressure, residence time, the composition of the gasification agent (water vapor, air or oxygen) and the equivalent ratio (ER). The use of several additives and catalysts has proven to be required to maximize the production of some of the desired compound and to reduce the emission of gaseous pollutants. The best experimental parameters to be used are dependent on the chosen structure of the gasifier and must also be adapted for each kind of biomass, depending on its chemical composition and physical characteristics.

The suitability of different types of biomass wastes for gasification has been studied by several authors. Forestry biomass has been largely gasified (Corella, 1999a, 1999b, Bridgwater 1995), but some other types of biomass wastes have also been studied, such as: sewage sludge, RDF (Residue Derived Fuel), olive oil bagasse, short rotation cultures, like cardoon and miscanthus (Paterson, 2002, Andre, 2005, Franco, 2003) and shells with different proveniences such as almond or coconut.

Bridgwater, 1995 reviews the potentialities of biomass gasification in general and wood in particular, emphasizing technology status and key uncertainties that are crucial to the success or failure of biomass gasification. Corella has a wide range of publications in the area of biomass gasification, studying different types of biomass, gasification experimental conditions and gas cleaning processes to achieve the production of gas with a wide range of energetic applications.

Bari, 2000 compared gasification in a small-scale installation of agricultural residues such as almond shells and wood, oak and Turkey oak. These biomass wastes led to different gas compositions both in organic compounds like tar and inorganic such as: NH_3, HCN, metals, etc. For instance almond shells led to much higher contents of tar and of ammonia, because woody biomass was richer in calcium than almond shells and calcium promoted a certain decomposition of ammonia.

Three types of forestry biomass were steam gasified by Franco et al. 2003: pinus pinaster (softwood), eucalyptus globulus and holm-oak (hardwood). The results obtained showed that it was possible to substitute on biomass species by another without main changes in fuel gas composition and for the three species studied the operating conditions were optimized for a gasification temperature around 830ºC and a steam/biomass ratio of 0.6 - 0.7 (w/w), as a gas richer in hydrogen and poorer in hydrocarbons and tar was produced.

As biomass wastes may have problems of availability all over the year, some authors have studied the possibility of replacing one biomass species by another, trying to keep as much as possible the characteristics of the gas produced. Paterson et al., 2002b, gasified in a pilot scale air blown reactor sewage sludge pellets and sewage sludge and coal blends and compared the results obtained with that produced during coal alone. No major operational problems were found when sewage sludge was co-gasified and the presence of sewage sludge increased both the calorific value of the gas and the fuel conversion in comparison to values achieved with coal alone. Therefore, sewage based materials proved to be suitable for gasification and their use could even improve the process performance.

Andre et al., 2005 studied gasification of olive oil bagasse, both alone and mixed with coal and observed that the increase of bagasse content rose tar and gaseous hydrocarbons contents in the fuel gas and both could be reduced by increasing gasification temperature and/or air flow rate. The use of dolomite in the gasification fluidization bed allowed decreasing tar content and rising gas yield, being the gas richer in hydrogen content, though no significant changes in gaseous hydrocarbons release was observed.

The production of great amounts of sewage sludge and the environmental problems that theirs disposal may cause led to the idea of gasifying this material to take profit of its appreciable energetic content. The results obtained so far have shown that sewage sludge gasification led to great production of gases with high heating values mainly due to great hydrocarbons contents. Wang et al., 2004 compared co-gasification and co-incineration of sewage sludge and observed that co-gasification presented a better performance than co-incineration. Paterson et al., 2002b also stated that sewage sludge gasification allowed raising both the calorific value of the fuel gas and the fuel conversion, in comparison with coal gasification, because methane content of the fuel gas was higher and therefore, the fuel gas produced showed high calorific value.

RDF presents a high energetic content and therefore, the possibility of gasifying this material has been studied. RDF usually has a considerable amount of plastics, the high calorific value and low moisture content of plastics wastes, are attractive characteristics for gasification, mainly when these wastes are mixed with others with low volatile contents and/or with high ash and sulfur contents.

Mixtures of wastes with different characteristics and compositions may allow taking profit of the advantageous properties of some wastes and at the same type diluting the undesirable characteristics of other wastes. By the right manipulation of these mixtures it is possible to increase the production of synthesis gas and decrease the release of undesirable compounds like tar, nitrogen and sulfur compounds emissions during their co-gasification.

Lately, the interest in gasifying short rotation cultures like cardoon or miscanthus has also increased. The growth of these cultures has been studied to maximize its production with the aim of using them as energetic cultures, either for combustion or gasification purposes. However the contents of these cultures in sodium, potassium and calcium should be closely controlled has they may lead to the formation of compounds with low melting temperatures, which may damage the reactor, due to bed sintering and may demand purging the bed more frequently to prevent this effect.

The same problem has also been identified during the gasification of bagasse wastes, especially those produced by olive oil production industries. However, the gasification of such wastes showed to be advantageous when compared to coal gasification, as reported by Andre et al., 2005.

When different hinds of biomass wastes were gasified at similar experimental conditions some changes in gas composition were obtained, as presented in Figure 1. Pine gasification produced the highest CO concentration and this tendency was also observed for bagasse gasification. However, pine gasification led to CO concentration 16% higher than those obtained during olive bagasse gasification, probably due to the higher oxygen content presented by pine in relation to that of olive bagasse. CO_2 compositions were produced either in presence of pine wastes or olive bagasse.

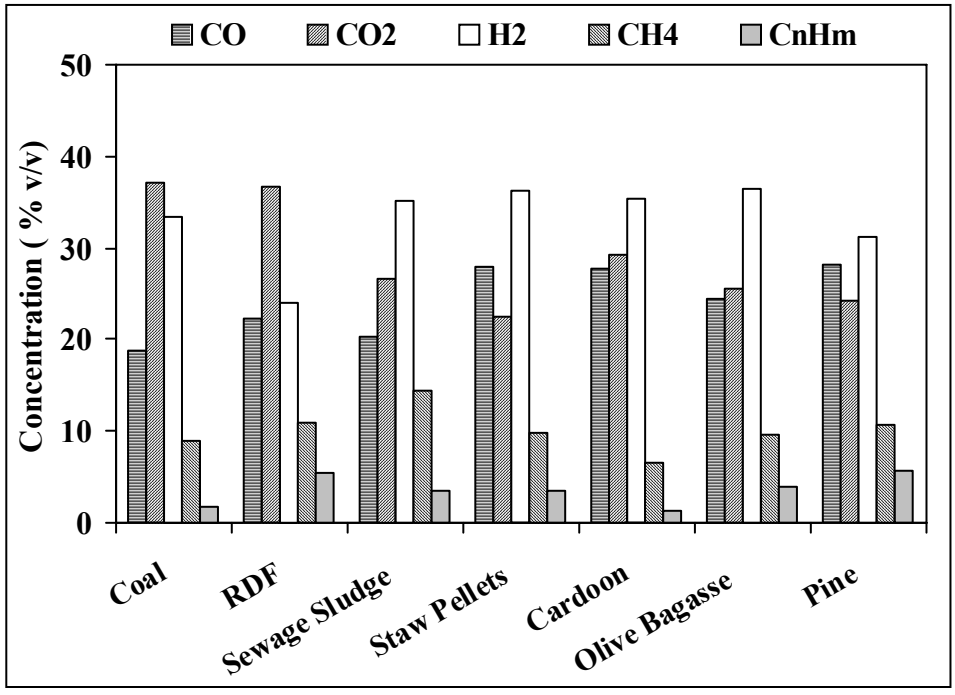

Figure 1. Gas composition obtained during gasification of different types of biomass wastes and Puertollano coal. Gasification temperature – 850ºC, steam/feedstock ratio – 1 (w/w) and O2/feedstock ratio – 0.6 (w/w).

Sewage sludge gasification led to the highest hydrocarbons concentrations of both CH_4 and C_nH_m and to low hydrogen content than that detected in the syngas produced by either pine or bagasse gasification. The lowest H_2 content was obtained when RDF was gasified, probably due to the high contents of CO_2 produced.

Similar gasification gas yields were produced in presence of similar amounts of wastes, independently of its type, therefore, gas yields seem to be more affected by the amount of waste than by its type. The opposite happened in relation to fuel gas HHV (higher heating value), which was much dependent on the type of waste gasified, as its value depended on gas composition. Therefore it was for RDF gasification that the highest fuel gas energetic content was obtained, due to the highest contents of hydrocarbons.

The presence of high contents of hydrocarbons is advantageous if the gas is going to be burnt, as it will increase its HHV. However, for other syngas end-uses, like fuel cells, it is necessary to decrease hydrocarbons contents, by different processes, as it will be discussed later. As some biomass wastes are seasonal and are not available during all months of the year, it is important to study the viability of substituting one type of wastes by another or of using mixtures of different types of biomass wastes, without major changes in the gasification installation. Due to this reason, some authors have studied the possibility of using mixtures of different types of wastes and mixtures of wastes with conventional fuels like coal (Pinto, 2008b, Pinto, 2007a). Pinto, 2008b studied co-gasification of sewage sludge mixed with biomass wastes (straw pellets) and compared the results obtained with either sewage sludge gasification or co-gasification of sewage sludge mixed with coal.

The increase of sewage sludge content in straw pellets blends allowed to increase CH_4 and C_nH_m concentrations in fuel gas of around 48 and 62%, respectively, Figure 2, probably due to straw pellets higher content of volatiles. The faster release of these compounds followed by their cracking and reforming reactions might have lead to lower hydrocarbons contents and also to the formation of H_2. In Figure 2 may be also observed the decrease in H_2 release with the rise of hydrocarbons concentrations. Co-gasification of coal and sewage sludge mixtures led to similar tendencies, as the rise of sewage sludge also led to a decrease in H_2 release and an increase in hydrocarbons concentrations, probably because coal volatile matter was higher than that of sewage sludge.

The increase of sewage sludge content in straw pellets blends also led to an increase in CO_2 release of around 55% and to a decrease in CO content of about 47%. The co-gasification of mixtures of sewage sludge and coal also showed that the rise of sewage sludge amount increased CO_2 release, whilst CO decreased, though the variations obtained were milder than those observed for sewage sludge and straw pellets blends, probably because oxygen contents of coal were the lowest. As the rise of CO_2 release with sewage sludge amount was followed by a decrease in H_2 content in the fuel gas, it was observed a cross over in H_2 and CO_2 curves for sewage sludge content of around 20% (w/w), for higher contents of sewage sludge the fuel gas was richer in CO_2 and for lower sewage sludge amounts the fuel gas was richer in H_2.

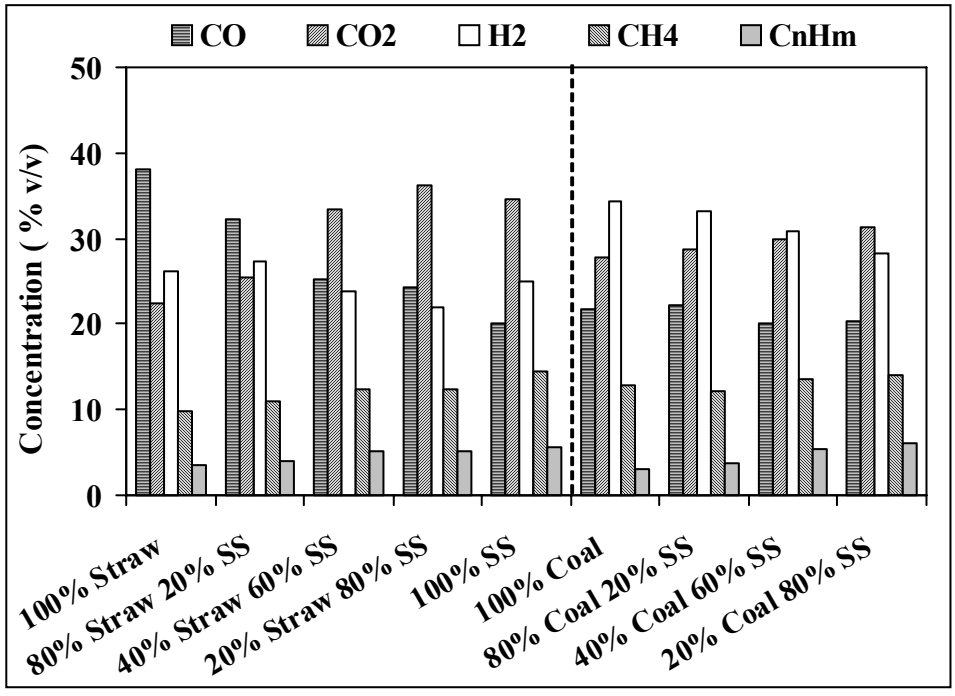

Figure 2. Effect of sewage sludge content on gas composition during co-gasification with straw pellets or with Puertollano coal. ER – 0.21, steam/feedstock ratio – 1 (w/w), temperature - 850ºC. SS – sewage sludge.

Though experimental conditions used by Wang et al., 2003 were quite different, it was also observed an intersection between H_2 and CO_2 curves for co-gasification of coal mixed

with sewage sludge. The results reported seem to show that the presence of sewage sludge tend to reverse Boudouard reaction (3).

The rise of sewage sludge content led to a lower gas production, though the fuel gas produced had a higher calorific value, probably due to the higher contents of hydrocarbons released, as hydrocarbons heat of combustion are much higher than that of CO or H_2. Sewage sludge gasification led to lower gas yields than those obtained with other wastes, like pine or bagasse wastes, probably due to the high ash content and the low volatile matter of sewage sludge (34.5% and 50.3%, respectively), therefore, sewage sludge might have produced less volatile matter than other waste mentioned.

The possibility of substituting biomass by a biomass and plastic blend was studied by Pinto et al., 2002 in a fluidized bed steam gasification reactor. The increase of PE amount in pine blends increased gas yield and H_2 release, up to values of 50% (v/v) and the contents of hydrocarbons in the fuel gas. The reduction of hydrocarbons could be achieved by rising gasification temperature, which also decreased tar and char and favored the formation of H_2. Co-gasification has proven to be a possible way of converting biomass and plastic undesirable wastes into fuel gases. The steam/waste mixture ratio seems to have a small effect on gas composition. Temperature is the parameter that most influenced gases composition. At 885ºC and in presence of 40% (w/w) of plastic, conversion to char was around 2%, whilst feedstock conversion to gas was around 90%. By the right manipulation of gasification experimental conditions it was possible to enhance the gas production and improve its composition and energetic content.

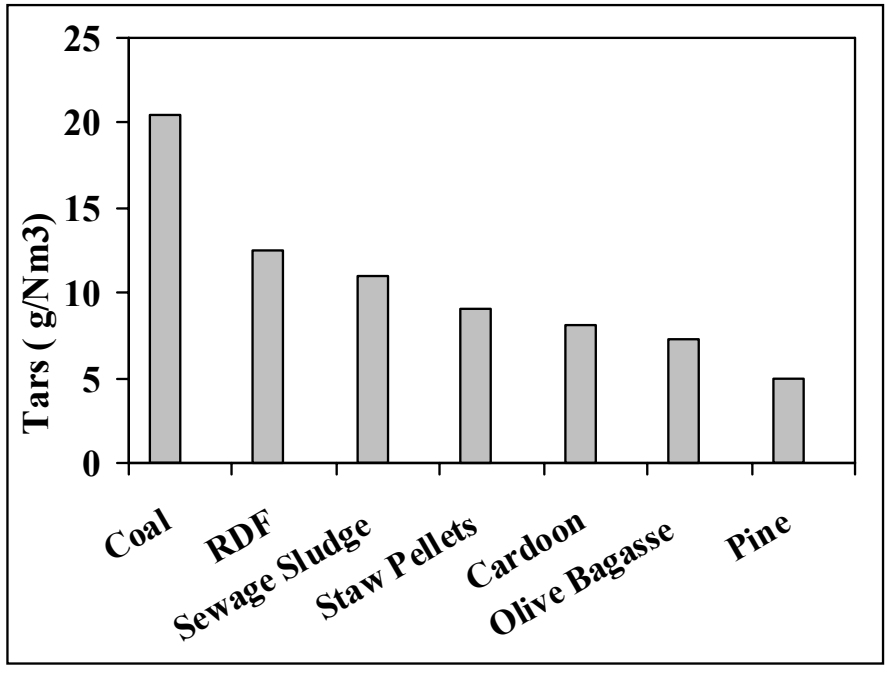

Figure 3. Tar content in fuel gas obtained by gasification of different types of biomass wastes and Puertollano coal. Gasification temperature – 850ºC, steam/feedstock ratio – 1 (w/w) and O_2/feedstock ratio – 0.6 (w/w).

Tar formation during gasification also depends on the type of waste. Pine and olive bagasse wastes gasification led to lower tar contents in the fuel gas than that produced by coal gasification, Figure 3. Gasification of wastes mixtures with PE (polyethylene) increased largely the formation of tar, which was rose further when higher amounts of PE were added to the wastes mixtures, probably due to the polymeric nature of PE, which broke into smaller fractions by thermal cracking and probably due to PE chemical structure, tar formed could have presented a polymerized structure, more difficult to destroy. When pine wastes substituted some of PE wastes a decrease in tar formation was observed.

As shown in Figure 3, bagasse gasification led to higher contents of tar than those produced with RDF and the gasification of mixtures of these two wastes led to tar contents that lay between those obtained when only one of these wastes was gasified.

3.2. Effect on Ammonia Formation

Due to sewage sludge high contents of nitrogen, sulfur and chlorine, gasification gas may also present high contents of several compounds of these elements, such as NH_3, H_2S and HCl, because of the reduction conditions of gasification. The formation of such compounds should be closely monitored and controlled during gasification, as they are pollutants precursors. A similar approach should be also followed during RDF gasification, as depending on theirs origin and composition, RDF may also contain high levels of undesirable elements, like nitrogen, sulfur, chlorine and heavy metals.

Several authors have studied the formation of nitrogen compounds during gasification and have stated that most of nitrogen was released to the gas phase as NH_3. Liu et al., 2003 reported that, besides N_2, NH_3 was the main nitrogen compound released to the fuel gas, as both HCN and NO emissions are at least one order smaller than NH_3 releases. NH_3 formation is a very complex issue, as it depends on several parameters, such as: gasification experimental conditions, nitrogen content of waste to be gasified and also the presence of several elements present in the feedstock mineral matter or even the reactor building metals, which may participate in forming and destruction NH_3 reactions. However, one of the most important parameters is the nitrogen content of biomass waste, as reported by Pinto et al., 2008c and Van der Drift et al., 2001.

NH_3 should be retained in the solid obtained after gasification, to decrease it release to the fuel gas. Liu et al., 2003 defined some of the chemical reactions that may retain nitrogen in the solid phase. NH_3 may be formed from nitrogen in char (char-N) through the reactions (16) to (18), but afterwards the NH_3 formed may be decomposed through reaction (19).

$$\text{char-N} + CO_2 \leftrightarrows NH_3 + \text{products} \quad (16)$$

$$\text{char-N} + H_2O \leftrightarrows NH_3 + \text{products} \quad (17)$$

$$\text{char-N} + H_2 \leftrightarrows NH_3 + \text{products} \quad (18)$$

$$NH_3 \leftrightarrows \tfrac{1}{2}\, N_2 + 3\, \tfrac{1}{2}\, H_2 \quad (19)$$

Van der Drift et al., 2001 measured NH_3 contents in the fuel gas that varied from 130 to 12500 ppmv, depending on the feedstock used: demolition wood (both pure and mixed with

sewage sludge and paper sludge), verge grass, railroad ties, cacao shells and different woody fuels. In general, wastes with high contents of nitrogen led to high NH_3 contents in the fuel gas, however, there were some exceptions, for instance demolition wood mixed with sewage sludge that presented the highest nitrogen content did not lead to the highest NH_3 content. These authors also stated that the release of NH_3 to the gas phase were in average about 60% of the nitrogen present in the fuel. Nevertheless, Tian et al., 2005 reported lower nitrogen conversions into NH_3, as only 14% of the nitrogen present in biomass was converted into NH_3. On the other hand, Paterson et al., 2002b observed that the release of NH_3 into the gas phase led to similar values contents both for sewage sludge gasification and for coal gasification, though sewage sludge had higher nitrogen content than coal.

Tian et al., 2006, studied the effect of ash or ash-forming species on the conversion of fuel-N during gasification of brown coal and a sugar cane trash. The results reported showed that the interaction of ash with char and/or volatiles could increases NH_3 yield and decreases HCN yield, though the conversion of one compound into the other could not be proven. The authors stated that some ash species could migrate into the char matrix to promote the formation of NH_3. Sodium impregnation of coal, either by NaCl or Na_2CO_3, favored interactions between Na loaded into the coal with volatiles, which could improve the formation of soot-N, which would be gasified to form NH_3.

Yu et al., 2007 investigated the effect of nitrogen chemical structures in the biomass fuels on the formation of NH_3, HCN and NO. Four biomass species: birch, Salix, Miscanthus, and Reed canary grass and Daw Mill coal were gasified at 0.4 MPa and 900 ºC. The percentage of the nitrogen retained in char was higher for coal than for the biomass species. The results reported showed that for all biomass fuels the main nitrogen heterocyclic compound was pyridine, but higher concentration of two-ring NHC in the tar were obtained in presence of higher fuel-nitrogen contents. According to these authors, the amount of N-fuel was not an important factor for NH_3 formation, as active hydrogen concentration in the reaccional medium, the intrinsic reactivity and internal surface area of the nascent char were key factors.

Zhao et al., 2003, used model chars to study the effect of Na, Ca and Fe on the formation of HCN and NH_3 during pyrolysis at 900 ºC and observed that a small percentage of N-fuel was converted into volatile-N as HCN and NH_3. Na favored the conversion of char-nitrogen to volatile-nitrogen at high temperature, while the effect of Ca and Fe was unimportant.

In Figure 4 may be analyzed the effect of biomass type and nitrogen content on NH_3 release to the fuel gas. NH_3 concentrations presented in Figure 4 refer to the total amount of NH_3, released to the fuel gas, though in installations with condensation system, more than 90% of the NH_3 released is usually kept in the condensation system, due to NH_3 solubility. NH_3 contents in the syngas, after the quenching system, were usually below 200 ppmv. (Pinto et al., 2007a).

Gasification of sewage sludge led to the highest NH_3 content, probably due to the highest nitrogen content of sewage sludge, in relation to that found in other wastes or coal, Table 2. The second high NH_3 contents were obtained for coal and bagasse gasification, probably due to the relatively high nitrogen contents of coal and bagasse, respectively, 2.2 and 2.1% daf (dry and ash free). However, the release of NH_3 during bagasse gasification was higher than that obtained for coal, probably because coal mineral matter might have favored the retention of nitrogen.

Table 2. Biomass wastes elemental composition

Elemental Analysis	Puertollano Coal	Sewage Sludge	Straw Pellets	RDF	Cardoon	Bagasse	Pine
Carbon (% daf)	81.8	55.8	49.3	56.0	50.8	55.1	50.6
Hydrogen (% daf)	5.6	7.4	6.2	8.1	5.8	6.5	6.4
Nitrogen (% daf)	2.2	7.4	0.77	0.1	0.7	2.1	0.2
Sulfur (% daf)	1.3	1.9	0.15	0.5	0.1	0.13	0.2
Chlorine (% daf)	< 0.08	0.14	0.28	0.06	0.5	0.14	0.07
Oxygen (% daf)	9.0	27.4	43.3	35.2	42.1	36.0	42.5

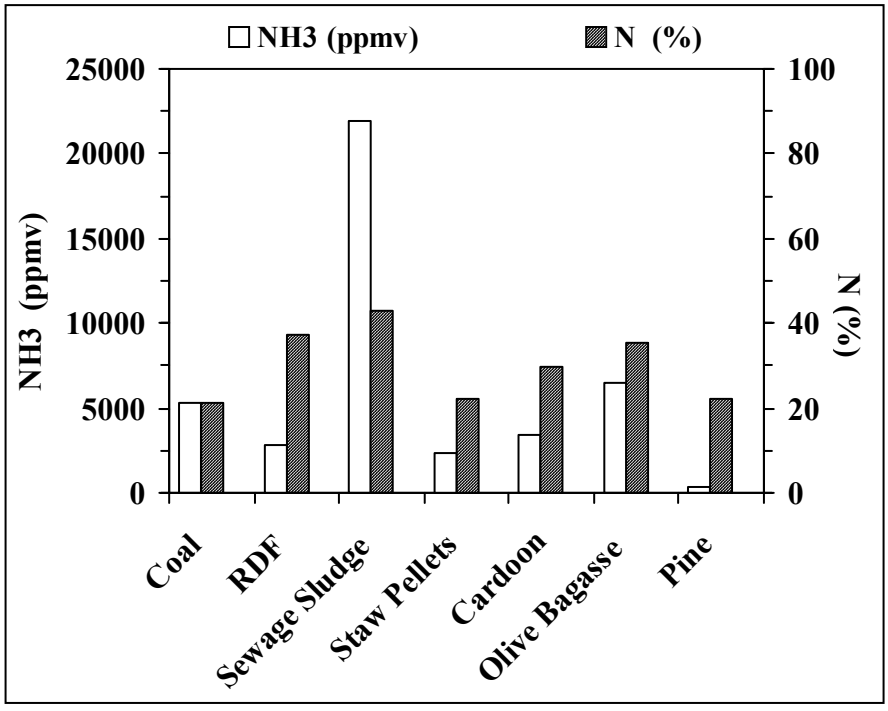

Figure 4. Effect of biomass type on NH_3 formation during gasification at 850ºC. Gasification temperature – 850ºC, steam/feedstock ratio – 1 (w/w) and O_2/feedstock ratio – 0.6 (w/w).

Although, cardoon and straw pellets presented similar nitrogen contents, the release of NH_3 was higher for cardoon gasification which shows that even if the amount of nitrogen in the feedstock is an important parameter, there are others that affect the formation and destruction of NH_3, as mentioned before.

Co-gasification of either RDF and coal mixtures or cardoon and coal blends showed that the increase of either RDF or cardoon led to the formation of lower NH_3 contents, probably because coal nitrogen amounts were higher than those found in either of these wastes, Table 2. In Figure 4 is also presented the percentage of nitrogen converted into NH_3, in relation to the amount in the feedstock, referred as N (%). The percentage of nitrogen converted into NH_3 varied between 20 and 40%, which means that most of nitrogen introduced in the gasifier was retained in the solid phase collected in the cyclone and inside the gasifier.

Pinto et al., 2008c, measured NH_3 release during co-gasification of sewage sludge mixed with straw pellets and observed that when the amount of straw pellets in the blend increased, there was a reduction in NH_3 concentrations in the fuel gas, probably due to low nitrogen contents of straw pellets. The percentage of nitrogen converted into NH_3, in relation to the amount present in the feedstock changed between 22 and 36%, which means that most of the nitrogen in the feedstock was retained in the solid phase, even when high amounts of sewage sludge were used in the blends and the release of NH_3 was higher than 20 000ppmv.

The main challenge of actual biomass gasification research work is the control and reduction of NH_3 compounds, either by experimental conditions optimization or by diluting the wastes with higher nitrogen contents with other with low levels of this element, as NH_3 presence is undesirable for most syngas end-uses, due to the formation of NO_x.

However, NH_3 formation and N partitioning in different phases may be a very complicated issue. Chars containing Fe and Ca and the gasification bed material may also have catalytic effect at high temperatures on the destruction of NH_3 from the fuel gas to N_2 over a reaction temperatures range of 700 to 900ºC. Even interactions with the reactor wall material may play an important role in NH_3 destruction, as reported by Tian et al. 2005.

3.3. Effect on Sulfides Formation

The release of H_2S during biomass gasification should also be measure and controlled, as this compound is a pollutant precursor and may also cause corrosion in pipes and equipment. During biomass gasification most sulfur was released as H_2S, as only, a much smaller amount was released as COS. According to Paasen et al. 2006, 70-90% of sulfur was released as H_2S, while only 3-10% could lead to COS.

Drift et al., 2001 gasified different biomass wastes and verified that, in general, the gasification of wastes with higher sulfur amounts led to the release of higher H_2S contents, however, some exceptions were also observed, as for instance in presence of sewage sludge. Though this waste presented the highest sulfur content, probably due to the high contents of some elements like calcium, some of the sulfur might have been retained in the solid phase.

Kuramochi et al., 2005 predicted HCl and H_2S emissions during gasification of several biomass fuels: demolition wood, verge grass, sewage sludge, bio-dried wood, railroad ties and cacao shells and analyzed the influence of biomass metal composition and gasification temperature on these compounds emission. H_2S concentrations ranged from 97 to 4000 ppmv for the different biomass fuels and a linear relationship between the maximum value of H_2S concentration and the sulfur content in the feedstock was obtained. However, sulfur retention in the solid phase could occur by reaction (20) if the feedstocks presented significant contents of some metals like Fe, Zn and Ca, being M: Ca, Zn, Fe, Mn, etc. As verge grass and cacao shells did not contain appreciable amounts of Zn and Fe sulfur retention was low..

$$MO + H_2S \leftrightarrows MS + H_2O \quad (20)$$

Moreover reactions (21) and (22) may also play an important role in the process of H_2S reduction, as the majority of sorbents or reagents occur in the form of oxides

$$MO + H_2 + CO \leftrightarrows M + H_2O + CO_2 \quad (21)$$

$$M + H_2S \leftrightarrows MS + H_2 \quad (22)$$

On the other hand, H_2S may react with iron oxides by reactions (23) to (25). Therefore, sulfur partition between solid and gas phases is a complicated issue that depends on several parameters, such as: the form in which sulfur was present, as sulfur existed in both organic and inorganic forms in the fuel, the presence of mineral matter in the feedstock and gasification experimental conditions.

$$Fe_3O_4 + H_2S \leftrightarrows FeS + Fe_2O_3 + H_2O \quad (23)$$

$$2Fe_2O_3 + H_2S + 2H_2 \leftrightarrows FeS + Fe_3O_4 + 2H_2O \quad (24)$$

$$2Fe_2O_3 + H_2S + 2CO \leftrightarrows FeS + Fe_3O_4 + 2CO_2 \quad (25)$$

In Figure 5 may be analyzed the effect of several biomass wastes with different sulfur contents on the formation of H_2S. Sewage sludge and coal presented the highest sulfur contents, Table 2, and probably because of that, the highest H_2S contents were obtained. However, sulfur content of sewage sludge was higher than that of coal, as shown in Table 2, but the H_2S released by sewage sludge gasification was lower than that formed by coal gasification, probably due to mineral matter of sewage sludge that might have retained sulfur in the solid phase. It was probably due to a similar reason that the H_2S released by RDF gasification was lower than those obtained by the gasification of straw pellets or cardoon, though it contained higher sulfur contents.

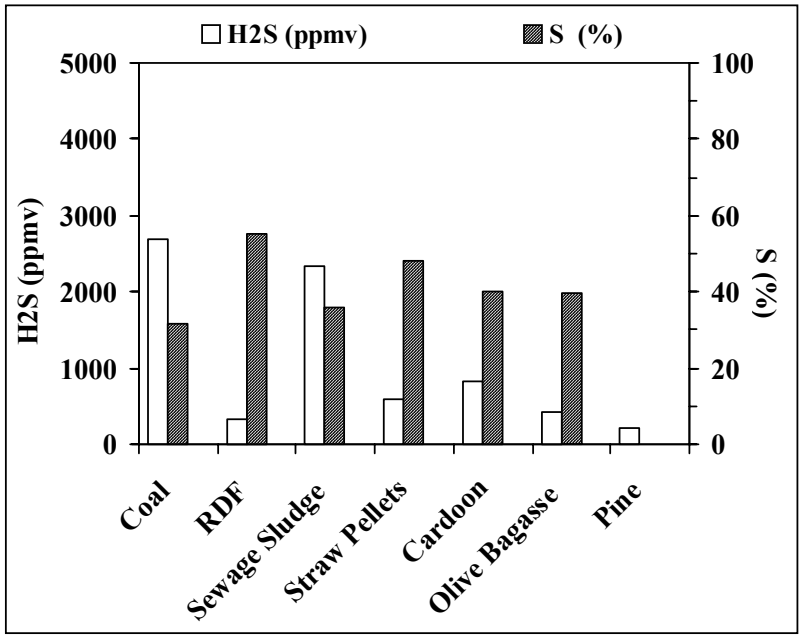

Figure 5. Effect of biomass type on H2S formation during gasification at 850ºC. Gasification temperature – 850ºC, steam/feedstock ratio – 1 (w/w) and O2/feedstock ratio – 0.6 (w/w).

H_2S contents obtained during sewage sludge gasification were lower than those reported by Kuramochi et al., 200, though the waste used these authors had lower sulfur content (1.5 %), probably because different experimental conditions were used, apart from that, different sewage sludge may present sulfur in different forms, organic or inorganic and may contain certain elements that might retain sulfur.

In Figure 5 may be observed that the percentage of sulfur released to the fuel gas, S (%), varied between 30 and 55%, the highest value was obtained for RDF, which agrees to the lowest release of H_2S, though the RDF sulfur was higher than that of other wastes. For most biomass wastes, retentions higher than 60% were obtained, even without the addition of any catalysts or sorbents.

Co-gasification of sewage sludge and straw pellets blends showed that the rise of sewage sludge amount led to an increase in H_2S concentrations, which agree with the higher sulfur content of sewage sludge.

3.4. Effect on Chlorides Formation

Measurements of HCl contents in gasification gas produced by different biomass wastes showed that in general, wastes with higher chlorine contents led to higher releases of HCl, however some exceptions were also observed, probably due to different elemental compositions presented by the wastes that might have reacted with chlorine to retain it in the solid phase. HCl formation during gasification is a complicated issue that depends on several factors, the form in which chlorine appears (organic or inorganic compounds) and its content in the feedstock are important parameters. But gasification operating conditions like: temperature, oxygen and steam contents and the presence of elements or compounds that might react with chlorine, leading to its retention in the solid phase, are also major important aspects.

Li et al., 2005, studied chlorine volatility during pyrolysis and gasification and observed that chlorine volatility could be controlled by the addition of CaO and process temperature. They also stated that the release of HCl was also affected by the content of other elements such as: Si, Al, K and heavy metals.

Wei et al. 2005, studied the gasification of three different biomass wastes: Danish straw, Swedish wood, and sewage sludge and observed that HCl release was affected by Na content and by its relative concentrations in relation to other elements. During wood and sewage sludge pyrolysis, nitrogen addition enhanced the formation of KCN(g) and NaCN(g) and reduced the release of K(g) and Na(g), which also affected the release of HCl.

Pinto et al., 2008b studied the release of HCl during co-gasification of straw pellets blended with sewage sludge. As straw pellets presented higher contents of chlorine, higher contents of HCl were obtained for co-gasification of sewage sludge and straw pellets blends than that when only sewage sludge was gasified. On the other hand, co-gasification of sewage sludge mixed with coal allowed decreasing the high contents of H_2S released during the gasification of only coal, probably because sewage sludge had lower sulfur content than the coal tested. Most chlorine released to the fuel gas was condensed in the condensation system.

Kuramochi et al., 2005 observed that the maximum concentration of HCl for different biomass fuels ranged from 0.1 to 800 ppmv. However, a linear relationship between the maximum value of HCl concentration and the chlorine content in the feedstock was not

found, probably because HCl concentration is affected by other elements such as heavy metals or alkali and alkaline earth metals. The formation of KCl or NaCl decreases the release of HCl at low temperatures. However, according to Kuramochi et al., 2005 predictions, sodium was consumed for the formation of sodium calcium or aluminum silicates at low temperatures and therefore, NaCl could only be formed in presence of high Na contents.

Co-gasification of different carbonaceous materials with a wide variety of composition may help to understand the behavior of the feedstocks and the synergetic effects during co-gasification process. Special care should be taken, when substituting one waste by another, as the formation of undesirable S, N and Cl compounds is most affected by the contents of these elements in the initial materials. Mixtures of different wastes could be made to take profit of the diluting effect of same wastes in relation to the formation of undesirable compounds. On the other hand, gasification installations should be enough flexible to allow an adjustment of gasification experimental conditions. When one waste is substituted by another, the addition of specific catalysts or sorbents could be also advisable to control the release of undesirable gas components.

The knowledge obtained by different wastes gasification and co-gasification of wastes mixtures will help to achieve a better management of wastes by taking advantageous of their energetic content, minimizing the undesirable features and at the same solving the problems related to wastes seasonability and shortage.

4. Effect of Experimental Conditions on Gasification Gas Components

4.1. Effect of Temperature

The temperature rise favored all the hydrocarbons further reactions, resulting in an increased conversion into hydrogen, trough cracking and reforming reactions. Decreases on CO_2 concentrations with the rise of temperature may be due to its consumption in the reforming reaction with methane, reaction (12) and also by other CO_2 reforming reactions of light hydrocarbons, reactions (13) and (14), which will increase with temperature. The water-gas shift reaction (7) could increase CO_2 concentrations, but the results obtained by Gil et al., 1999, also seem to indicate that the CO_2 consuming reactions would be more significant than the shift reaction (7).

Syngas obtained at higher gasification temperatures, as it loses its methane and other hydrocarbon contents, present a lower HHV. This effect may usually be compensated by the rise verified on gas yields, resulting in an increase of net energetic conversion of the gasification process.

The higher gas yields obtained at higher gasification temperature may be due to three factors: a) an increased production of gas on the initial pyrolysis phase; b) higher extension on the steam reforming and cracking reactions of tar and heavier hydrocarbons and c) rise of char gasification reaction, which is favored by higher temperatures.

The same trends are reported by many authors, indicating an increase on gas yield and decrease of its HHV, at higher temperatures, even on gasification studies including diverse

feedstocks and installations. This can be found on several papers related to biomass gasification, for instance those presented by Gil et al., 1999, Herguido et al., 1992.

Co-gasification of biomass mixed with plastic wastes was studied by Pinto et al., 2002. Although temperature increases originated a reduction on hydrocarbon contents of syngas, these amounts were still high enough to compromise some the gas possible end-uses. On the gasification of wastes with a high fraction of plastic residues, CH_4 and other hydrocarbons concentrations were around 10% and 2% (v/v) at the maximum tested temperature of 900ºC. The choice of this higher temperature should be carefully planned as it may impose strict restrictions on the choice of construction materials and the problems associated with ash melting which depend on the mineral matter content of the chosen fuel.

The results obtained by a large number of gasification studies have shown that temperatures in the range of 850–900ºC should be selected. To achieve a further reduction on hydrocarbon contents, in that temperature range a higher oxygen flow rate should also be used, even with the corresponding decrease of the gas HHV.

The general conclusions over the effect of each parameter are similar on the results obtained by different authors, even considering some differences due to different determination methods and experimental conditions used by different authors. It is always found that a high biomass conversion and a low tar concentration on the gas required the use of gasification temperatures higher than 800ºC. The effect of temperature on gas composition is very clear. Typical variations obtained in a fluidized bed gasifier when the temperature changed from 750 to 850ºC were higher H_2 and CO concentrations, a small reduction on CO_2 amounts and reductions on CH_4 and C_2H_2 concentration, as reported by Narvaéz et al., 1996. These authors also reported a marked decrease of around 74% on tar concentration.

Kinoshita et al., 1994, presented similar conclusions on tar emissions and also reported that the total number of chemical species present in tar was reduced at higher temperatures. Oxygen containing compounds like phenol, cresol and benzofuran were only present in noticeable amounts at temperatures below 800ºC. The use of temperatures higher than 850ºC caused the destruction of tar components with aromatic structures like: benzene, naphthalene or phenanthrene.

Similar studies made under pyrolysis conditions by Yu et al., 1997, showed that tar destruction caused by a temperature increase corresponded to the formation of more gaseous species. By increasing the temperature between 700 to 900ºC, it was possible to obtain a tar reduction of around 40%. These authors found that the oxygen containing species was significantly reduced, as also were the species presenting 1 or 2 aromatic rings (except naphthalene). However, both naphthalene and other species containing 3 and 4 aromatic rings showed a marked increase, which was attributed to a conversion from phenolic compounds to aromatic, promoted by higher temperatures.

The use of higher temperatures presents somewhat dissimilar effects as some benefic like an increase on gas yields, char conversion and decrease on hydrocarbons, tar and other pollutants but it may also cause a reduction on gas heating value and increase the risk of if sintering of the sand bed material.

Liu et al., 2003 proposed two pathways for tar formation from biomass, reactions (26) and (27)

Primary pyrolysis:

$$\text{biomass} \rightarrow \text{char} + \text{primary tar} + \text{gases } (CO + CO_2 + CH_4 + H_2O) \quad (26)$$

Secondary pyrolysis:

$$\text{primary tar} \rightarrow \text{secondary tar} + \text{gases } (CO + CO_2 + CH_4 + C_2H_x + H_2) \quad (27)$$

Tar content in fuel gas depends on tar formation and tar cracking. Reaction (26) can be promoted by thermal cracking and reactions with O_2 and H_2O with or without a catalyst. The rise of temperature favors tar cracking.

Several authors have stated that NH_3 concentration in the fuel gas could be achieved by the rise of gasification temperature, because the thermodynamic decomposition of NH_3 is an endothermic reaction. Tian et al., 2002 studied the release of nitrogen compounds during fluidised-bed and fixed-bed pyrolysis of sewage sludge with 8.1 % daf of nitrogen and observed that both HCN and NH_3 were the NO_x precursors. The main route for HCN formation was the thermal cracking of volatiles. At temperatures lower than 400 to 500 ºC, amino structures in the sewage sludge were responsible for the formation of NH_3, while at higher temperatures the hydrogenation of N-containing structures in the pyrolysed solid particles was responsible for the formation of NH_3. The same authors, in a more recent publication, Tian et al., 2005, studied nitrogen conversion during the pyrolysis and gasification of a cane trash with 0.3 % daf of nitrogen and verified three major routes of NH_3 formation: hydrolysis of N-containing structures in the solid phase, thermal cracking and gasification of solid nascent char and thermal cracking and reforming of volatile-N.

Paterson et al. 2002a observed that the addition of steam and its conversion into H_2 promoted the formation of NH_3. In the absence of limestone that acted as a sorbent, the increase of temperature from 800 to 970ºC decreased the release of NH_3, due to its decomposition through reaction (19). In presence of a sorbent, NH_3 concentration had a peak at around 880ºC, probably, because two opposite effects happened with sorbent, NH_3 destruction favored by higher temperatures and NH_3 formation, hich according to the authors could be caused by the limestone, s the peak was not observed in the absence of sorbent.

Liu et al., 2003, predicted the reduction of NO, NH_3 and HCN emissions with the rise of temperature, which agree with the experimental results of Zhou et al., 2000.

Experimental results showed that the rise of temperature from 750º to 850ºC during sewage sludge co-gasification allowed decreasing NH_3 reduction of around 30%, lasting constant for a higher temperature. However, this value was lower than that reported by Paterson et al., 2002a who mentioned NH_3 reductions of around 50%, for the temperature range from 770º to 950ºC. These differences might be due to different experimental conditions and different sewage sludge composition used in each work. The increase of temperature during co-gasification of cardoon also led to a decrease of NH_3 content in the syngas. On the other hand, when feedstocks with lower nitrogen contents, like RDF or pine were gasified, the effect of temperature was not so notorious. As low NH_3 contents were formed at the lowest temperature tested, 750ºC, the effect of rising temperature was much milder. For sewage sludge gasification the rise of temperature up to 850ºC led to a decrease in the percentage of nitrogen present in the fuel gas phase from 25 to 38%, which means that most N-biomass was retained in the solid phase. For RDF or pine gasification no important

changes were observed in the percentage of nitrogen released to the gas phase, which agrees with the mild variations of NH_3 content in the fuel gas.

According to several authors, the rise of gasification temperature causes H_2S formation and increases its release into the fuel gas. Experimental results showed that the increase of temperature during sewage sludge gasification led to an increase in H_2S in the syngas of about 30%. This tendency was not obtained when temperature was increased during the gasification of other types of biomass wastes, like pine, cardoon, straw pellets and bagasse, probably due to the smaller sulfur contents in these wastes. However, when the temperature rose from 750º to 850ºC during co-gasification of coal blended with 40 % (w/w) of sewage sludge, an increase of about 30% in H_2S in the syngas, was obtained. These results agree with those reported by Kuramochi et al., 2005. These authors predictions showed that during gasification of different biomass wastes, the production of H_2S reached a maximum in the temperature range of 750ºC to 850ºC. The rise of H_2S concentration was due to FeS decomposition, though the decompositions temperatures seemed to be dependent on the biomass waste studied and on the presence of other elements that promoted FeS destruction. FeS was transformed to $Ca_2FeSi_2O_7$ and this occurred at 823 K for demolition wood, whereas for the railroad ties it happened at 973 K. Contrary to what was observed for ZnS, the decomposition of FeS was dependent on the production of $Ca_2FeSi_2O_7$. FeS decomposition was found to be related to the Fe content in the feedstock and Kuramochi et al., 2005 found a linear relationship between the two, which may be useful for the predictions of H_2S emission from biomass gasification.

The effect of rising the temperature during the co-gasification of different biomass wastes showed that for sewage sludge no significant changes in HCl concentrations were observed, this tendency was also predicted by Wei et al., 2005. When sodium content was greater than that of potassium and in presence of high contents of silicon and aluminum in sludge, sodium was retained in ash as aluminosilicate and it was only likely to be released at temperatures higher than that normally used in fluidized bed gasification, higher than 1027 ºC. The rise of temperature during gasification of biomass wastes with low chlorine contents, like pine and RDF, had no significant changes in HCl concentrations, probably due to the low chlorine concentrations and also to the low contents of mineral matter presented in these wastes. The highest reduction of gaseous HCl with the rise of temperature was observed during co-gasification of cardoon. At the lowest temperature tested, 750ºC high HCl concentrations were obtained, while at 850ºC HCl contents were similar to those produced by other types of wastes, probably, chlorine reactions with mineral matter presented in the bed when cardoon was used were favored by the rise of temperature, but after certain retention of chlorine these reactions might have slowed down, by lower amounts of reactants.

Kuramochi et al. [15] predicted that for gasification temperatures below 550ºC, HCl emissions were low, due to the presence of alkaline earth metals that could trap chlorine in the solid phase. Below this temperature, the formation of KCl or NaCl allowed decreasing the release of HCl to the fuel gas, at higher temperatures, the solid KCl was partially vaporized and also HCl and NaCl were vaporized. Consequently, the formation of KCl or NaCl may play an important role in chlorine retention, but only at temperatures lower than that usually used in gasification. However, even at lower temperatures, the formation of KCl depends on the amounts of Si and Al, as they may also react with K and therefore, decrease the amount available to react with Cl. For high temperatures, the variation of HCl release with temperature also depended on the presence of elements, such as: K, Al, Na and Si, and the

competition among them to react with chloride. In the case of biomass fuels with aluminum, $KAlSiO_4$ or $KAlSi_2O_6$ were predominantly formed. These authors suggested blending potassium-rich biomass with potassium-poor biomass to reduce the HCl emission during gasification, through the formation of KCl, however, KCl will also vaporize at the normal used temperatures for gasification.

Keown et al., 2005 pyrolysed sugar cane bagasse and cane trash to study the volatilization of alkali and alkaline earth metallic species (mainly K, Na, Mg and Ca) and found that by rising the temperature from 500 to 900 ºC, at slow heating rate, caused little changes in the volatilization of Na, K, Mg and Ca for both bagasse and cane trash. The opposite was observed for the fast heating rate, as the effects of increasing temperature strongly depended on the biomass substrate. The increase of temperature from 500 to 900 ºC during bagasse pylolysis, significantly reduced the retention of Na, K, Mg and Ca. On the other hand, the rise of temperature from 500 to 900 ºC during cane trash pylolysis, led to an increase in the volatilization of K and Na, but the retentions of Mg and Ca in the cane trash char were not affected by the heating rate. The retentions of Ca and Mg in cane trash char were higher than those in the bagasse char, which was not expected, due to the higher Cl content in cane trash than in bagasse, being against the normal assumption that Cl in biomass is likely to lead to higher volatilization of Na, K, Mg and Ca. Experimental results reported by several authors have shown the extensive volatilization of Cl, as only around 1% of Cl originally present in feedstock was retained in the char. K like other alkali and metal alkali metals are released into the gas phase mainly as KCl during gasification of biomass.

It is difficult to understand completely the formation and destruction of HCl and metal chlorides, due to the several parameters that affect these reactions and also because of some of then may act in opposite directions. Therefore, the effect of temperature on HCl release into the syngas is a complicated issue that needs further research work.

4.2. Effect of Oxygen Flow Rate

Several different agents may be used during biomass gasification like: oxygen or air, water vapor or carbon dioxide. The choice of the gasification agent allows the selection of some of the fundamental characteristics of the gas that will be produced, like its composition, the presence of inert gases and its calorific value.

The use of air as gasification agent causes a large reduction on the gas heating value due to the dilution caused by Nitrogen. Narvaéz et al., 1996, studied biomass gasification with air at 800ºC, with and ER of 0.35 and obtained a gaseous mixture with 10% H_2, 14%CO, 15% CO_2 (on volumetric basis) and a major fraction of nitrogen. These authors increased ER values to achieve a reduction on tar emissions, through the increased availability of oxygen on the pyrolysis zone, these conditions also caused reductions on H_2 and CO with an increase of CO_2 and the consequent decrease on gas heating value.

Since the use of air, dilutes the gas obtained, an alternative approach uses water vapor as gasification agent, as it allows the production of gaseous mixtures with more than 50% of H_2 and practically no nitrogen. Herguido et al., 1992, studied the effect of steam/biomass ratio on gasification of particle sizes on the range of 0.5-2.5 mm. By increasing this ratio, H_2 and CO_2 concentrations were raised, while CO amounts were decreased. Hydrocarbons like methane were slightly reduced, whilst heavier species like C_2H_2, C_2H_4 and C_2H_6 remained steady. Tar

amounts presented a large reduction, but there was also a marked reduction on gas heating value, corresponding to the decrease of CO.

The higher production of H_2 can be explained by the effect of steam on the extension of water gas reaction (4) and (5), water-gas shift reaction (7) and steam reforming (8) to (11). However in these conditions the gasification process is endothermic, requiring an external energy source, which can increase the process complexity and operation costs.

Consequently, the use of oxygen and steam mixtures has been proposed as gasification agents for biomass. The use of oxygen can supply the system with the required energy for the global gasification process, turning it self-sustaining. The work of Aznar et al., 1997, points out that the use of these mixtures on biomass gasification, gave a reduction of 85% of tar emission by increasing (steam+O_2)/biomass mass ratio from 0.7 to 1.2.

Gil et al, 1997, studied biomass gasification with steam and oxygen and recommended a H_2O/O_2 molar ratio of 3.0. These authors found that increasing (steam+O_2)/biomass mass ratio from 0.6 to 1.7 caused a reduction on H_2 and CO, an increase on CO_2 and a small reduction on CH_4 and on other gaseous hydrocarbons. These changes also caused reductions on tar emissions. The optimum gasification conditions included temperatures on the range of 800-860ºC and a (steam+O_2)/biomass mass ratio between 0.8 and 1.2. The same authors compared their results with those obtained by Narvaéz et al., 1996 and Herguido et al., 1992 and concluded that using other similar conditions, the use of only steam gave higher tar formation, while the use of air gave minimum tar amounts. Intermediate values were obtained by the use of steam and O_2 mixtures, as gasification agent.

The use of CO_2 as gasification agent has also being considered a possibility, as it is already one of the existing species on the gas mixture obtained with the gasification process. The work of Minkova et al., 2000, using mixtures of steam and CO_2 indicated that they can promote the CO_2 reforming reactions (12) to (14). Garcia et al., 2000, studied catalytic gasification with CO_2 using a Ni/AL catalyst. These authors found that, in relation to the use of steam, the combined effect of CO_2 and the catalyst increased the formation of H_2 and CO, decreased tar emissions and also lighter hydrocarbons (CH_4, C_2H_2, C_2H_4 and C_2H_6). There was a net CO_2 consumption, as the use of a CO_2/biomass ratio of 1.16 gave a reduction on CO_2 amounts. To avoid carbon deposition on the catalyst it should be used an even higher amount of CO_2 to promote Boudouard reaction (3).

The rise of ER favored tar oxidation reactions and therefore, a decrease in tar release into the syngas was observed. As a decrease in gaseous hydrocarbons was also observed, the fuel gas produced had a lower calorific value when higher ER values were used. A small decrease in tar contents was also observed with the rise of steam flow rate, keeping constant the bed fluidization rate, as tar steam reforming reactions were favored. However, this reduction was smaller than expected, since combustion reactions seem to be more predominant then steam reforming ones and therefore, more responsible for tar content, as reported by Andre et al., 2005.

During co-gasification of sewage sludge at of 850 ºC, the rise of ER values allowed decreasing NH_3 release of around 33%. These results agree with those of literature. Paterson et al. 2002a studied the effect coal/air ration on NH_3 formation and observed that the increase of this ration promoted the formation of NH_3, due to the input of coal volatiles and N-fuel. A large increase in NH_3 formation was also observed with the rise of steam, probably due to reaction (17). The reverse of reaction (19) may also favored the formation of NH_3, by H_2

action resulting from steam decomposition. However, the H_2 formed during pyrolysis did not seem to have a similar effect.

Liu et al., 2003, stated that both NH_3 and HCN contents decreased with the rise of ER due to the NH_3 decomposition and the reduction of NO by NH_3 in the presence of oxygen. During gasification with air, an ER increase from 0.2 to 0.4 led to a reduction in NH_3 release. These authors also stated that an increase in biomass moisture resulted in NH_3 destruction, which agrees with the experimental results found by Drift and Doorn, 2000. Zhou et al., 2000, also reported that the increase of ER from 0.17 to 0.25 during biomass gasification allowed decreasing NH_3 release. As the production of nitrous oxide was found to be insignificant, bellow about 10 ppmv, according to these authors fuel-N released to the gaseous phase could mostly be converted to N_2 in the presence of char, H_2 and CO.

On the other hand, it was observed that when biomass wastes with low nitrogen contents, like cardoon or RDF were gasified, the rise of ER increased NH_3 content till a maximum value was achieved, and then NH_3 content decreased. For cardoon gasification this maximum was obtained for an ER value of 0.35, but for RDF, the maximum NH_3 content was obtained for an ER of 0.2. These results might be due to higher char conversions and to higher releases of NH_3 when more oxygen was present in the reaction medium, but for higher ER values more oxygen might be available to react with nitrogen and to form NO_x instead of NH_3. It was also observed that the amount of char decreased with the rise of ER and similar char contents were obtained for the two highest ER values, either for cardoon or for RDF.

On the other hand, apart from the ER values, the oxygen/steam ratio may be also an important issue, as an increase of steam in the gasification medium favors the formation of NH_3 as also reported by Tian, 2005.

As most forestry biomass wastes has low contents of sulfur, it is of no use to increase ER values to achieve small reductions of H_2S, having in mind that this measure will also decrease gas calorific value. Due to this reason, there are not in literature many studies about the decrease of H_2S during biomass gasification, being most of the information found about this subject referred to coal gasification. However, some other biomass wastes like sewage sludge and some RDF may present high sulfur contents and therefore, care shall be taken in controlling and decreasing the release of H_2S during these wastes gasification. The increase of ER till values about 0.29 during co-gasification of sewage sludge decreased the H_2S concentration measured in the syngas of about 45%, probably, due to the oxidation of S-feedstock and conversion into SO_2. Although, there was a clear decrease in H_2S content during sewage sludge gasification, it was compensated by the formation of SO_2, therefore, no great changes were observed in the percentage of sulfur released to the gas phase, S (%). However, the SO_2 formed could have been further reduced by H_2 and CH_4, in the presence of steam, by reactions (28) and (29), as reported by Nicholas et al., 1989, due to the high contents of both H_2 and CH_4 in the reaction medium.

$$SO_2 + 2\ H_2 \leftrightarrows H_2S + H_2O \quad (28)$$

$$SO_2 + CH_4 \leftrightarrows H_2S + H_2 + CO_2 \quad (29)$$

However, SO_2 conversion after its formation was not detected experimentally. The results obtained, regarding the effect of ER in H_2S release agree with those reported by Nichols et al., 1989 during oxygen blown coal gasification. These authors stated that the increase of ER

above 0.5 led to a reduction in H_2S and CS_2 in the syngas accompanied by higher SO_2 and COS formation, due to a greater level of oxidation. However, the oxidation reaction can be influenced by several factors: the presence of steam in the gasifier, the pressure in the gasifier and the recirculation of reactants and products inside the gasifier, as reported by Price et al., 1983.

It is expected that the rise of ER would lead to lower HCl contents, as its destruction would be favored by oxidation reactions, however, the effect of ER in HCl destruction is a difficult subject, as it is affected by many different parameters, some of which act in opposite directions.

Sewage sludge gasification studies showed that the rise of ER value up to 0.3 led to a decrease in chlorine content in the syngas, probably due the partial oxidation reactions. In general, low percentages of chlorine in the gas phase were obtained, which meant high retention in the solid phase, probably, because of the high quantities of Fe, K, Na and Ca in sewage sludge that might have reacted with chlorine. The rise of ER during cardoon gasification also led to a reduction in HCl release into the syngas when ER values increased till ER of around 0.2. For both wastes further increase of ER values led to an increase in the gaseous chloride detected in the syngas, probably because, the increase of oxygen flow rate promoted the reaction of further amounts of char, as detected experimentally and therefore, more chloride was released to the gas phase. It is predictable that the rise of ER till values higher than 0.4 would lead to a reduction of gaseous HCl, as the addition of more oxygen would promote its destruction.

Wei et al., 2005, gasified three different biomass wastes: Danish straw, Swedish wood, and sewage sludge and observed that the increase of air excess improved the release of HCl(g), KOH(g), or NaOH(g) and decreased the formation of KCl(g), NaCl(g), K(g), or Na(g), because the excess air promoted the formation of H2O and of radical OH-, which are likely to favor reaction (30) and (31).

$$KCl(g) + H_2O \leftrightarrows KOH(g) + HCl(g) \quad (30)$$

$$K(g) + OH \leftrightarrows KOH(g) \quad (31)$$

Wei et al., 2005, stated that the release of chlorine was very dependent on the concentration of alkali metals in the gasification system and that the volatilization of these metals may depend more on the concentration of chorine than on the concentration of the metals, which could form stable compounds with chorine and therefore, a small increases of ER could not be enough for an effective reduction of HCl.

4.3. Effect of Adding a Catalyst or Sorbent

4.3.1. Gas Main Components

One of the best ways to improve the quality of the obtained gaseous mixture is using catalysts. Most available information recommend the use of catalysts to decrease the amount of tar and other hydrocarbons that result from the pyrolysis products obtained after an incomplete gasification of coal and biomass mixtures. Some of these catalysts can also affect the cracking, methanation and steam reforming reactions.

Most recent works suggest the use of catalysts to decrease the formation of other harmful products like ammonia, sulfur compounds, chloride and other halides, that can compromise the use of the obtained syngas in turbines engines or fuel cells. The formation of these compounds will be especially troublesome during the gasification of biomass or wastes containing higher amounts of nitrogen, sulfur, halogens or other elements that can originate these deleterious compounds. The work done on catalytic tar removal was also extended to the effect of some of these catalysts on the removal of sulfur and chlorine compounds.

The choice of a suitable catalyst must focus, not only on its action on the conversion of tar and hydrocarbons, but also on the resistance to deactivation, on the possibility of its regeneration, mechanical resistance to erosion and cost. On gasification installations it is also important that the chosen catalyst presents some effect on methane reforming reactions, while also increases the ratio H_2/CO.

Corella et al., 2004a, refer that the catalyst cost may by a restrictive factor on its choice, as long distance transport of a catalyst, even if it has an initially low cost, may prevent its use. Alternatively, these authors suggest that gasification installations should be located near mines where naturally occurring minerals with good catalytic activity were accessible.

Another determining factor on tar formation is related on the feeding system of the gasifier. In updraft gasifiers there is a larger amount of tar formed during fuel pyrolysis that is released without being decomposed. In this case fuel conversion to tar can be up to 10%, as indicated by Bridgwater, 1994. In downdraft reactors the final gas will have lower tar amounts, since the initial formed compounds will pass through a hotter gasifier zone were they decompose, achieving tar formations of less than 1%. According to Bridgwater, 1994 fluidized bed gasifiers will present intermediate tar concentrations.

In general, catalysts are used directly in the gasification reactor, but some authors indicate that it could be possible to increase its efficiency using an additional reactor to treat the gasification gases. In these conditions, the deactivation of the catalyst will be smaller as it will not contact with char and unconverted fuel that could be deposited on its surface. However the studies presented by Corella et al., 1999a, have shown that dolomite was more efficient while it was used inside the main reactor, as it could act directly on the decomposition of the primary tar. Otherwise, in a secondary reactor, the tar initial formed might suffer some polymerization and were more refractory and more difficult to decompose. In contrast, these authors defended that the presence of a secondary reactor at a high temperature has the advantage of increasing the total reaction volume and could facilitate all the homogeneous gas reactions.

Corella et al., 1999a, verified that the use of dolomite on a secondary reactor caused only a small advantage on tar decomposition, in comparison on its use inside the main reactor. However, for gas uses where the allowed tar levels are minimal (less than 1g/Nm^3) it will be best the use of secondary reactor, containing a more active catalyst, for example a nickel-based one.

These secondary reactors may contain the reactor in a fixed or fluidized bed, but in the latter case it needs to be considered the catalyst erosion resistance. In these reactors an additional reactant flow can be used, like steam or CO_2 as it is described by Sutton et al., 2001a. With these conditions, it is possible to promote, among others, the hydrocarbons reforming reactions (11) and (13), increasing the concentration of H_2 and CO on the final gas mixture.

More recent studies have shown that the more efficient solution results from the use of both methods simultaneously. Catalysts used inside the gasification reactor may be lower cost minerals, which will not be reused. These catalysts aim a reduction of tar content of the primary gas, but are not very efficient on the reduction of methane and other hydrocarbons. On the secondary reactors, it can be used more expensive and effective catalysts that will act on a cleaner gas, promoting a further reduction on tar concentration, but also decomposing methane and other hydrocarbons through activation of reactions (8) to (14).

Several different catalysts have been tried both for coal and biomass gasification, however the assessment of the results obtained by different research teams is not straightforward, as the experimental conditions are different, including the use of different kinds of coal and biomass and the gasification reactors often present diverging characteristics. Furthermore, different sampling and analysis methods have been used, as there is not a single standard on results determination for gasification systems. An expert group discussed this aspect and elaborated a protocol to define standard methods for tar sampling and analysis, which did not reach the required consensus, as some authors questioned its validity, considering that it did not guarantee the reproducibility of experimental results. There is even an additional difficulty that arises from different methods to define what it is referred by the generic term of tar.

The catalysts commonly used on gasification studies can be divided into three large classes, namely: dolomite, olivine and other natural minerals, nickel based catalysts and more expensive catalysts containing many other metals.

Use of Dolomite as Catalyst

One of the first gasification catalysts was limestone, as is reported by Devi et al., 2003, with the advantage that this mineral avoids bed agglomeration. One of the most used catalysts is dolomite (MgO•CaO after calcination), due to its low cost and proven activity on tar decomposition reactions. Experimental results on tar reduction have been obtained and reported by several authors, as it is presented by Sutton et al., 2001 and Devi et al., 2003. It is necessary to highlight the large number of papers published by the gasification groups from the Madrid and Zaragoza Universities in Spain where the catalytic gasification of biomass using dolomite was much studied.

The amount of tar reduction promoted by dolomite depends on the experimental conditions, being reported by Narvaez et al., 1996 a tar reduction of around 40%, while Corella et al., 1999b indicated that under favorable conditions it was possible to achieve reductions of tar up to 80%, but without noticeable variation on the concentrations of methane and other gaseous hydrocarbons.

Dolomite also presents another advantage as it decreases the agglomeration of the fluidized bed material. It presents the shortcoming of a low mechanical resistance, with the possible erosion of its particles, resulting in an increase entrainment of catalyst fine particles that must be removed before a further treatment of the gas.

The results obtained by different authors using dolomite are not always in agreement as these catalysts are obtained from different mineral sources and present different mineral compositions. Usually dolomite presents a mass composition of around 30% CaO, 21% MgO and 45% CO_2 but may also present many other metal oxides, containing namely Fe, Al, Si etc. These minerals may also present a large range on surface areas and pore distribution

sizes. Dolomite is generally used after calcinations, where the initial CO_2 is released and the catalytic effect of the different metals is enhanced.

Orio et al., 1997 compared the catalytic action on biomass gasification of several Spanish dolomites with different compositions and origins. It was reported that the presence of higher Fe_2O_3 amounts and larger pore sizes increased tar conversions and gave higher gas yields. The effect of pore size was not always consistent since in some cases there was coke deposition inside the pores and the catalytic effect was accordingly reduced. The obtained results did not include major variations on the final gas compositions indicating that the used dolomites presented a similar low effect on the conversion of gaseous hydrocarbons.

Orio et al., 1997, Delgado et al., 1997, and Vassilatos et al., 1992, studied the effect of several experimental parameters on the catalytic action of dolomite, verifying that higher temperatures improve the results of this catalyst. Vassilatos et al., 1992, verified that even after the use of dolomite at a temperature in the range of 800-900ºC, the resulting gas still contained naphthalene, being the most abundant tar species, the presence of this compound indicated that dolomite was not effective enough to guarantee the complete conversion of tar. Several other authors, as reported by Sutton et al., 2001a also studied the catalytic activity of dolomite using model compounds usually found in tar like toluene, cyclohexane and benzene.

Different authors like Vassilatos et al., 1992, and Sutton et al., 2001a, also found that dolomite was easily deactivated, especially inside fluidized beds, due to the loss of mechanical resistance and coke deposition. This last effect was decreased when steam was used as gasification agent because it could promote coke reforming reactions. The presence of earth-alkaline oxides resulting from the dolomite calcination also catalyzed the conversion of coke. The use of higher air flow rates also promoted coke oxidation at the surface or on the inner pores, decreasing the deactivation of dolomite.

Use of Olivine as Catalyst

Olivine presents the chemical formula (Mg, Fe)•$2SiO_4$, with a Mg/Fe ratio of 9/1. Olivine is another mineral species that has been used to catalyze tar decomposition reactions. Some authors indicate that it presents an higher catalytic activity than dolomite, while other assert the opposite. Rapagnà et al., 2000, referred that olivine present a reduction of up to 90% on tar emissions with an activity similar to calcinated dolomite. However, olivine has the drawback that it is less abundant than dolomite and as many countries do not have olivine sources, the operation costs for gasification units would be increased if dependent on olivine imports.

Corella et al., 2004a, compared the catalytic action of dolomite and olivine on biomass gasification and confirmed that dolomite was 1.4 times more effective on tar conversion but dolomite presented the shortcoming of producing 4 to 6 times more fines during gasification than olivine. This observation turns more difficult the catalyst choice, depending on the compromise between the requirements of lower tar amounts or lower solids to be present on the outgoing gas. Corella et al., 2004a, also found similar gas compositions when dolomite or olivine where used or even without any of those catalyst, depending on the right choice of experimental conditions, including the type of biomass gasified. The addition of dolomite or olivine did not cause any problems on particle agglomeration, because the used temperatures were below 900ºC. The authors deem that neither dolomite nor olivine can be considered as the best catalysts for biomass gasification.

Studying the catalyst effect on NH_3 formation, Corella et al., 2004a, found that olivine was better choice than dolomite, as it led to lower NH_3 concentrations. However, the action of both catalysts was more ambiguous that in the case of tar conversion, as the presence of iron oxide on the catalyst is known to catalyze NH_3 synthesis from N_2 and H_2.

To increase olivine catalytic activity some authors have enriched it with other metals like nickel, as this species presents a good activity on tar conversion. Corella et al., 2004a, used a nickel enriched olivine with a mass fraction of 3.7% of Ni. While this catalyst presented a good activity on tar conversion, the best results were obtained only on steam gasification, with a fluidized bed of 100% of olivine. On air gasification with a silica sand fluidized bed the catalyst activity was severely reduced. This catalyst presented also a fast deactivation, requiring the use of a system for periodical regeneration. This could be achieved by the use of a system containing two parallel fluidized beds, where the gasification and regeneration could happen in sequence.

It is not clear if dolomite catalytic activity is better or wore when it is calcinated, before being added to the system. Calcination may change both the chemical composition and the physical properties of the catalyst, affecting its catalytic activity. Corella et al., 2004a, compared the use of natural olivine with olivine calcinated at 1500ºC. It was reported that calcination destructed the porous structure of olivine, reducing its activity on tar decomposition. With these results the authors disavow the calcination of olivine.

However, other authors like Devi et al., 2005, refer that olivine, after calcination at 900ºC for a long time, presents higher catalytic activity. The use of olivine, calcinated at 900ºC during 10h led to naphthalene conversions higher than 80%, significantly higher than that obtained with natural olivine.

Use of Other Minerals as Catalysts

Besides dolomite and olivine several other mineral have been used as catalysts for gasification reactions. The comparison between the results of different authors is not always easy, as the results obtained from each research group uses different experimental techniques and conditions, while they also use minerals with diverse geological origin, chemical composition and pore size distribution.

Delgado et al., 1996, compared the catalytic action of different calcium containing minerals with a commercial catalyst and with an inert material, on tar reduction from gases obtained with biomass gasification. The reported results show that the commercial catalyst presented the highest activity, being followed by calcinated dolomite > calcinated calcite > calcinated magnesite. The catalytic activity could still be improved by the use of higher temperatures and higher gas residence times.

In a later work, Delgado et al., 1997, also compared different minerals, reporting that the same trend observed for tar reduction was also verified for gas yields: calcinated dolomite > calcinated calcite > calcinated magnesite. These three catalysts however presented similar effects on the final gas composition. The authors also reported that catalytic activity was very dependent on surface area BET, what could help to explain the different results reported by different authors, as those areas will depend not only on the original mineral, but also on the experimental parameters used during calcinations like: temperature, time, atmosphere used, among others.

Corella et al., 2004a, also studied biomass gasification, comparing the catalytic activity of dolomite with other minerals and observed that, although calcinated calcite (CaO) and

calcinated magnesite (MgO) presented some activity on tar reduction, the best results were always obtained with calcinated dolomite.

Sutton et al, 2001, refer that the catalytic action of different carbonates and other minerals on biomass gasification was the following: potassium carbonate > sodium carbonate > trona– $Na_3H(CO_3)_2 \cdot 2H_2O$ > borax–$Na_2B_4O_7 \cdot 10H_2O$. While all the catalyst favored gas production it was not observed many differences on gas composition. Regardless of its highest activity, potassium carbonate presented the negative aspect of promoting the agglomeration of the particles inside reactor and increased the erosion of the reactor wall.

Regarding catalyst deactivation, Sutton et al, 2001, refer that it was better to impregnate the catalyst on biomass instead of using a simple mixture, as it could reduce the deactivation associated with coke deposition on catalyst surface and also decrease particle agglomeration. The mineral matter collected after biomass gasification was also used as catalyst for the gasification of biomass and coal, as indicated by Sutton et al, 2001.

This procedure enabled the reutilization of a sub-product of the gasification process itself. This mineral matter is usually mainly composed by 44.3 % of CaO, 15% MgO and 14.5% of K_2O (in a mass basis). It could increase coal reactivity by a factor of 9 and biomass reactivity by a factor of 32, in comparison to the use of inert materials. This difference on the obtained results for these two fuels was attributed by the authors to the self-catalytic effect of the mineral matter of the coal used.

Devi et al., 2003, compared the results obtained by different authors that also used the char obtained from gasification on a secondary reactor, to catalyze tar decomposition reactions and reported the very good results obtained at a temperature of 950ºC.

Encinar et al., 1998 studied the use of different materials on the gasification of wastes from wine production industry. The used materials were LiCl, NaCl, KCl, KCO_3, $AlCl_2 \cdot 6H_2O$ and $ZnCl_2$ which were all added with the mass corresponding to 5% of the metal. Except KCl, all the materials gave an increase on gas and char yields with the highest gas yields obtained with KCO_3. The presence of zinc favored H_2 production and as also reported by Sutton et al, 2001, the increase of zinc concentration originated higher char productions and lower liquids and gas yields, with the exception of H_2.

Use of Nickel Based Catalysts

All the reforming reactions with and without steam can be catalyzed by elements from groups 8, 9 and 10 (formerly group VIII) of the Periodic Table, being nickel the most used metal in industry to catalyze the reforming of natural gas and light or heavy naphtha. According to Corella et al., 2004a, nickel promotes the dissociation of H_2O, forming OH• radicals, which act on the opening of aromatic and poly-aromatic rings that mainly constitute tar.

Yoshiniri et al., 1984, compared the catalytic activity of different metallic oxides like V_2O_5, Cr_2O_3, Mn_2O_3, Fe_2O_3, CoO, NiO, CuO, MoO_3 supported in Al_2O_3. While, it was verified that all of these oxides increased the gas yield, with different gas compositions, NiO was the catalyst that presented the highest catalytic activity. Although, these authors did not determine tar amounts, they verified that this catalyst improved the product distribution and the calorific value of the obtained gas.

Several other authors have also tested the catalytic effect of different nickel compounds on the gasification of biomass or coal, using either compounds synthesized on the laboratory or commercial catalysts usually used on the industry. Wang et al., 1998, studied some

commercial catalysts. Aznar et al., 1993, tested the commercial catalysts R-67-7H and RKS-1, on a secondary reactor to promote tar reduction of gases obtained by biomass gasification. It is reported that despite the obvious catalytic effect, their life time was very short due to coke deposition on the catalyst surface. Aznar et al., 1993, also studied the catalytic effect of other commercial catalyst supplied by companies like BASF, ICI-Katalco, UCI and Haldor Topsøe, some of them were generally used as catalysts for the steam reforming reactions of light hydrocarbons, while others presented high efficiency on reforming reactions of heavier hydrocarbons, like naphtha. The obtained results revealed that the latter ones were more effective for tar reduction.

Baker et al., 1987, also studied the catalytic effect of several commercial catalysts containing nickel, on the reduction of tar on gases obtained by biomass gasification. It was found that while all the catalyst presented a positive effect, some of them were more easily deactivated by carbon deposition. In this case the regeneration of some of the catalyst proved difficult, as some material have the tendency to sinterization and to the corresponding activity loss. Some studies also compared the catalytic effect when the catalyst was used on the primary gasification reactor or on a secondary reactor, being reported that in the former case, despite the catalytic activity being initially higher, the catalyst deactivation was much faster than in the latter case.

Yamaguchi et al., 1986, also verified that the studied nickel catalyst, supported in alumina, presented a fast activity loss during the duration of the experimental work, due to both the effects of carbon deposition and catalyst sinterization.

Kinoshita et al., 1995, observed that catalyst activity was improved by the use of higher temperatures and longer residence times and concluded that the amounts of both tar and hydrocarbon contents on the gas obtained from biomass gasification could be decreased to acceptable levels using the appropriate values for the different experimental conditions like: temperature, ER and residence time. However, the use of catalyst could present the negative outcome of increasing operation costs and decreasing the gas heating value.

Some other authors synthesized the catalysts studied for biomass gasification. Garcia et al., 1998, synthesized several nickel catalysts on alumina supports. These authors studied the need for a preliminary reduction of the catalyst with H_2, but verified that the reducing atmosphere of the gasification process turned that operation unnecessary.

Other authors studied the enrichment of the nickel catalysts using other metals like magnesium or potassium as additives. Arauzo et al., 1997, used magnesium to increase the catalyst mechanical resistance to attrition. Garcia et al., 2002, synthesized several nickel and magnesium catalysts supported in alumina and used them for the reduction of tar content obtained in biomass gasification. It was observed that the best results were obtained with $NiMgAl_2O_5$ followed by $NiMgAl_4O_8$, verifying that the former catalyst also presented the higher stability and the highest initial activity.

Richardson and Gray, 1997, tested biomass gasification using nickel and molybdenum catalysts enriched with alkaline metals, added as KNO_3, KOH, NaOH and LiOH. These species should decrease the superficial acidity, increasing the catalyst activity and reducing coke deposition. However, KNO_3 was not effective on acidity neutralization, contributing instead to catalyst poisoning at higher concentrations. The other chemicals have proved effective on acidity reduction but did not have effect on coke deposition.

Bangala et al., 1998, also studied the catalytic activity of a nickel catalyst over an alumina support, after impregnation with MgO, TiO_2 or La_2O_3. The mass fraction was varied

between 5 to 20%, being observed that gas yield increased for values of nickel up to 15%, decreasing afterwards, while coke deposition always increased with higher nickel fractions. From the impregnated materials, La_2O_3 originated the highest gas yields and the largest reduction on coke deposition.

Caballero et al., 2000, studied the catalytic effect of three commercial catalysts used on steam reforming reactions, identified as BASF G1-50, ICI 46-1, and Topsøe R-67. These catalysts were tested at pilot scale to decompose tar obtained during biomass gasification on a fluidized bed and proved to be effective on tar reduction to amounts around 10 mg/Nm^3.

The work done by Wang et al., 1999, also revealed that the use of nickel based catalysts on a secondary reactor could also decrease the initial values of NH_3 to values up to 95%. Several other authors, mentioned by Devi et al., 2003, also verified that nickel containing catalysts could be effective on both tar and NH_3 reduction, as long as that it was used in a secondary reactor.

The main drawback presented by nickel catalysts is the activity loss associated with coke deposition and H_2S poisoning. These problems can be reduced by either an increase on operating temperature or preferably by the use of an intermediate reactor containing dolomite that could promote a pre-treatment of the gasification gases, before their introduction in the reactor containing a nickel catalyst. This technique was suggested by Baker et al., 1987, Devi et al., 2003 and Corella et al., 2004a.

Use of Other Catalysts

Other authors have studied the use of catalysts prepared from chemicals that can be considered too expensive, at least for their use on gasification installations with an acceptable economical viability.

Rapagná et al., 2002, prepared a tri-metal catalyst containing La-Ni-Fe, which was used on a fixed bed gasifier to promote CO_2 reforming reactions. It was observed a conversion of roughly 90% of tar at a temperature of 800ºC. The used catalyst had the chemical formula $LaNi_{0.3}Fe_{0.7}O_3$ and showed a strong interaction between nickel and the oxide phase that permitted the formation of small nickel particles on the catalyst surface that avoided coke deposition and enabled catalyst regeneration by calcination. The use of this catalyst gave increased gas yields, a marked decrease on tar formation, lower methane contents and higher hydrogen concentrations.

Martinez et al., 2003, also studied the catalytic effect of Ni-Al-La on biomass gasification reactions. The authors prepared 3 catalysts always with a nickel mass fraction of 33% and different amounts of La and Al. All these catalysts have proven effective for their direct use on a fluidized bed gasifier, without significant elutriation or erosion. The amounts of CO, CO_2, CH_4, C_2 and the gas yield obtained with the Ni-Al-La catalyst were higher than those obtained when a Ni-Al catalyst was used, even though not significant changes were observed on H_2 concentration. The use of Ni-Al-La as catalyst for CO_2 reforming reactions, studied by thermogravimetry originated lower coke deposits than those obtained with a Ni-Al catalyst.

Asadullah et al., 2003, have used a secondary reactor to promote the catalytic tar decomposition on gases obtained from wood gasification, using a catalyst containing $Rh/CeO_2/SiO_2$. This system enabled to obtain higher conversions of the fuel carbon to gas and higher CO, H_2 and CH_4 than when those produced when only one reactor was used. Asadullah et al., 2004, referred that tar contents on the gas leaving the secondary reactor were low enough to allow their use on gas turbines, even from gases obtained at lower

temperatures than usually used, between 823 and 973 K. As almost all the initial carbon was converted to the gas phase, there was practically no coke deposition and so the catalyst was not deactivated. A serious disadvantage of this catalyst was its very high cost that completely prohibited its use on gasification installations at a pilot or industrial scale. The studies reported by Asadullah et al., 2004 were only made at a reduced scale, being only used about 3g of the $Rh/CeO_2/SiO_2$ catalyst.

4.3.2. NH_3 Reduction

Gasification of pine, sewage sludge and bagasse in presence of dolomite and olivine showed that NH_3 contents measured in presence of olivine, either natural or calcinated, were lower than those obtained with dolomite, probably due to iron content of olivine.

The results obtained by Dou et al. 2002 also showed that the Fe-based catalyst removed about 35% of NH_3. Corella et al. 2004 studied the effect of dolomite and olivine during biomass gasification and found that NH_3 content in the fuel gas was higher with dolomite than with olivine. Dolomite iron content was lower than that of olivine and though iron oxides can catalyze the reaction of N_2 and H_2, the results obtained seem to show that iron oxide content did not seem to be a decisive factor in the NH_3 amount released to the gasification gas.

According to these authors, as dolomite was more active for tar cracking than olivine, dolomite would crack more N-tar than olivine, hence producing more NH_3. This hypothesis also allowed explaining why dolomite was more efficient in reducing NH_3 contents in presence of pine wastes and less capable of that in presence of sewage sludge, as higher tar contents were also produced with this last waste.

The highest NH_3 reductions were achieved when a Ni-Mg catalyst was used during gasification of different types of wastes: pine, bagasse, sewage sludge and straw pellets. Reductions between 45% and 55%, were obtained depending on biomass waste tested. The second low NH_3 concentrations were obtained when a Ni-dolomite catalyst was used during gasification, this catalyst allowed NH_3 reductions of around 30 to 40%. These results agree with those reported by Dou et al. 2002, who reported that the Ni-based catalysts had higher activity, and more than 88% of NH_3 present in the feed gas was removed.

4.3.3. H_2S Removal

The presence of Ca-based sorbents, like limestone, dolomite or olivine has been proved to be effective in retaining sulfur in the gasifier ash and in producing a cleaner syngas.

The effect of either olivine or dolomite in H_2S reduction was studied during gasification of several biomass wastes. The presence of natural olivine in the gasification bed did not lead to great reductions in H_2S content in the fuel gas. As mentioned before, § 4.3.1, olivine contains iron and Najjar et al. 1995 stated that iron compounds promoted sulfur retention inside the gasifier, due to the formation of a new major oxysulfide phase, in addition to the silicate one. However, the presence of olivine did not lead to significant sulfur retentions in the solid phase, probably, this process did not occur to a significant extent and/or the iron content in olivine was not high enough to achieve further sulfur capture.

Calcinated olivine should be more effective in H_2S reductions, because through calcination different metallic compounds are converted into their oxides, which could favored sulfur retention, as metallic sulfides, MS, according to reaction (20), M being mainly Ca, Fe and Mg. However, the performance of calcinated olivine in sulfur was not always better than

that of natural olivine, depending on the type of biomass gasified, sometimes it was even worst.

The highest reductions in H_2S content in the syngas were obtained in presence of dolomite for all the biomass wastes gasified, being the percentage of gaseous sulfur lower than 10% for all the feedstocks studied. Dolomite was calcinated prior to its utilization, therefore, its main component was CaO, which according to reaction (20), M being Ca, could have reacted with H_2S to form CaS that remained in the gasification bed. The use of Co and Mo oxides in the gasification bed did not affect the H_2S content in the gas. Therefore, sulfur retentions in the solid phase were similar to those observed in the absence of catalyst. The same happened when Ni-Mg oxides were used during gasification of different biomass wastes.

These experimental results were coherent and agreed with those reported by several authors, even if different fuels were studied. Xu et al. 2005 reported that in the presence of CaO, higher retention of sulfur in the solid phase could be achieved, probably due to the formation of CaS. This was also proven by Sage and Welford 1997, as during co-gasification of sludge with coal, the sulfur retention reached 96% in the presence of dolomite. Similar results were obtained by Paterson et al. 2002, who achieved around 87% of sulfur retention in the solid phase with the addition of dolomite.

Khan, 1989 reported that the addition of CaO significantly reduced the release of H_2S into the gaseous phase; however, the use of $CaCO_3$ had relatively low influence, because due to the reduction conditions of gasification, significant calcination of $CaCO_3$ to CaO did not occur. According to Khan, 1989, the addition of 10% of dolomite allowed great reductions of H_2S in the gaseous phase, usually higher than 90%. The release of sulfur compounds both in tar and gas phase could be decreased and controlled by the use of inorganic additives containing Ca, Fe, Mg and Si compounds.

Park et al. 2005 studied different additives based on metal oxides containing Fe, Zn, Ni and Co for hot gas desulphurization and stated that metal sulfides (MS) produced from the H_2S reaction with metal oxides, could further react either with CO, which is a major component of syngas, to produce COS or with H_2O to produce SO_2, which decreased sulfur retention inside the gasifier.

Tijmensen et al. 2000 reported that, though Fe, Zn and Mn oxides have a strong affinity for H_2S, these oxides might be less resistant to the reaction with H_2 or CO as compared with alkaline earth oxides. The removal of H_2S through reactions with Fe_2O_3, or Fe_3O_4 could take place by reactions (23) to (25). These reactions could be repeated until the complete consumption of all the iron oxides, however, these reactions could be reversed by the presence of steam and CO_2 in hot gases and then affect sulfur retention. It is due to this fact that zinc ferrites ($ZnO.xFe_2O_3$) and zinc titanates ($ZnO.xTiO_2$) have shown to be more strong sorbents for desulfurisation, as reported by Zevenhoven et al. 2004.

4.3.4. HCl Destruction

The effect of different catalysts or sorbents during several biomass wastes gasification was analyzed. For all wastes studied: pine, straw, bagasse and sewage sludge the use of CoO and MoO catalyst did not le to significant changes in either gaseous HCl content or in chlorine retention in the solid phase. A similar situation was also observed in presence of Ni-Mg based catalyst. It was also tested a ZnO commercial catalysts, but no great reductions in HCl were obtained, probably because the catalyst was supplied as pellets, which after some

time were covered by dust, due to coke deposition, which prevented catalyst action. On the other hand, ZnO could have reacted with HCl, according to reaction (32), whose equilibrium might have been affected by the steam added to the gasifier. On the other hand, at the gasification temperature $ZnCl_2$ was liquid and due to its significant vapor pressure, it could have escaped from the sorbent.

$$ZnO + 2HCl \leftrightarrows ZnCl_2 + H_2O \quad (32)$$

Moreover, some of the $ZnCl_2$ formed by reaction (32) might also have reacted with H_2S, through reaction (33), due to H_2S presence in the reaction medium, especially when sewage sludge was gasified. Gibbs free energy and equilibrium constant values of reaction (33) at various temperatures, calculated by Gupta et al., 2000, showed that the $ZnCl_2$ reduction by reaction with H_2S to form ZnS was strongly favored at a temperature lower than 650 °C, leading to the formation of more HCl.

$$ZnCl_2 + H_2S \leftrightarrows ZnS + 2\ HCl \quad (33)$$

At the temperatures normally used in gasification, $ZnCl_2$ is probably in a liquid phase, which could have favored more reactions with H_2S than with solid ZnO, thus leading to further reductions of H_2S concentration. On the other hand, according to Park et al. 2006, ZnO could also react with H_2 and CO from the fuel gas through reactions (34) and (35). Hence, the metallic zinc gradually diffused to the surface and vaporized, for this reason and to improve ZnO performance, some inorganic oxides, like TiO_2, have been added to increase ZnO stability, mechanical strength and capacity of retention.

$$ZnO + H_2 \rightarrow Zn + H_2O \quad (34)$$

$$ZnO + CO \rightarrow ZnC + O_2 \quad (35)$$

The use of natural olivine during gasification of several biomass wastes, like: pine, straw, bagasse of sewage sludge, led to small decreases in HCl content, usually lower than 15%. Natural olivine analysis showed the presence of FeO(OH), which could have reacted with HCl, by reaction (36). FeO(OH) might have been destructed during the olivine calcination and converted into iron oxide and further formation of silicates. Probably due to this reason, the compound was not detected in calcinated olivine and its effect in HCl reduction was lower than that observed with natural olivine.

$$FeO(OH) + 3\ HCl \leftrightarrows FeCl_3 + 2\ H_2O \quad (36)$$

For all the catalysts or sorbents tested, dolomite led to the lowest HCl contents in the syngas, allowing reduction between 45 and 65%, depending on biomass waste composition. Thus, the percentage of chlorine released to the gaseous phase varied between 30% and 35%, which means that chlorine retention in the solid phase were higher than 65%. The action of Ni-dolomite during gasification was also studied, the percentage of chlorine released to the gaseous phase varied between 50 and 55%, against the 30-35% obtained in presence of

dolomite. As the presence of Ni-Mg catalyst did not affect the retention of chlorine, it is expected that the reductions obtained with Ni-dolomite were due to dolomite.

Dolomite main compounds are CaO and $Ca(OH)_2$, which could have reacted with HCl, by reactions (37) and (38) and thus retaining $CaCl_2$ in the solids. As $CaCl_2$ starts to decompose at 740 ºC and gasification tests were done at 850 ºC, some of the $CaCl_2$ decomposed by the reverse of reactions (37) and (38), might have released some HCl, which could then have caused a decrease in chlorine retention in the solid phase. Reactions (37) and (38) might also have been reversed by the steam introduced in the gasifier, which could explain why no higher chlorine retentions were obtained. HCl formation and the direction of reaction (37) and (38) could be affected by the content of other elements such as: Si, Al, alkaline earth metals and heavy metals, as they might compete with CaO to react with HCl. For instance, the presence of K in the feedstock could produce gaseous KCl instead of HCl, but this would also depend on the content of other elements and the competition among them to react with chlorine.

$$CaO + 2\ HCl \leftrightarrows CaCl_2 + H_2O \quad (37)$$

$$Ca(OH)_2 + 2\ HCl \leftrightarrows CaCl_2 + 2\ H_2O \quad (38)$$

Chlorine retention is a complicated issue affected by many parameters, for instance, $CaC1_2$ has a melting point at 772 ºC, and the lowest liquid temperature for the $CaC1_2$-CaO system is 750 ºC with a eutectic composition of about 6 % (mol) CaO. Therefore, a liquid phase of $CaCl_2$ saturated with CaO might be formed at gasification temperatures, which could have reduced the sorption capacity of CaO. In addition, the sorption capacity of CaO might also have been reduced by the reversibility of reaction (37) and (38) at high temperature, causing the release of HCl, as stated by Weinell et al. 1992. In spite of chemical reactions, physical properties of solids, namely particle size and specific area may also affect the amount of chlorine retention in the solid phase. According to Weinell et al. 1992, the surface area only had a minor effect on the final conversion of HCl at high temperatures and for $S_{BET} > 12\ m^2/g$.

In fact, there are many different phenomena occurring during gasification and some of them act in opposite directions, thus making difficult the complete understanding of the complex reactions that may occur.

5. PROCESSES FOR REDUCING ASH AGGLOMERATION

Apart from biomass forestry, other biomass wastes like agro-residues contain alkali metals such as: potassium and sodium, but also some silicon, alkali earth metals like calcium, chlorine and sulfur. Due to these elements, during agro-residues gasification may occur ash agglomeration and sintering, which may provoke erosion and corrosion in the equipment used.

Biomass wastes with high contents of sodium and potassium are especially dangerous, due to their great tendency to ash agglomeration. These metals break the Si–O–Si bond of silica and form silicates or alkali sulfates by reacting also with sulfur. The presence of

chlorine increases the mobility of potassium, as most of it is as KCl and promotes the mentioned reactions. The melting points of these compounds are below 700ºC and tend to deposit in reactor walls and in particles surface, which lead to sintering and defluidization, decreasing the heat transfer coefficients, limiting gas flow and reactor efficiency and at the end lead to plant shut-down. At large scale the formation of big rocks that causes erosion in reactors walls can even occur (Averlakis et al., 2002a, Averlakis et al., 2005).

Ash agglomeration can be better controlled and prevented in fluidized bed gasification, due to the lower gasification temperatures used and also due to better uniformity of temperature profiles achieved in fluidized beds. The lower gasification temperatures used allow reducing the volatilization of alkali metals, thus producing a syngas with better quality.

Ash-related problems can be reduced by biomass pre-treatments like leaching and fractionation, which efficiency depends on biomass type and characteristics. By water leaching is removed the water-soluble and ion exchangeable inorganic elements such as: K, Na, Ca, Cl and S. In mechanical fractionation, biomass wastes are ground and then shacked to obtain different fractions. Averlakis et al., 2002b divided the initial feedstock into two fractions, with particle sizes higher and lower than 1 mm.

As reported by Averlakis et al., 2002a, wheat straw have low water leaching efficiency for alkali metals, chlorine and sulfur, probably because the complex structure of straw difficult alkali metals leaching. However, for olive bagasse, water leaching could avoid significantly agglomeration and deposition problems, as almost of all alkali metals, chlorine and sulfur were removed, SEM-EDX analysis (scanning electronic microscopy with energy dispersive X-ray spectroscopy) showed that calcium was the main remaining element. Corn was moderately affected by the leaching process, as though the amounts of alkali metals, chlorine and sulfur decreased the remaining quantities were still enough to cause ash related problems.

Though mechanical fractionation could decrease biomass ash content of around 50%, the still remaining amount would also create ash related problems. Averlakis et al., 2005 fractionation pre-treatment of peach stones allowed decreasing ash content, but worse elemental composition was obtained with higher potassium contents, which led to significant increases in both the size and the strength of the deposits. Leaching pre-treatment of peach stones led to significant removals of alkali metals and chlorine from the ash, reducing both the size and strength of the deposits.

The best results reported by Averlakis, 2002b were obtained with combining fractionation and leaching, as the ash content was reduced and ash elemental composition was improved. However, these pre-treatments have the disadvantage of increasing operating costs.

6. HOT SYNGAS CLEANING PROCESSES

It is possible to control syngas composition and quality through optimization of biomass gasification process by the procedures previously described. However, for some kinds of wastes and also depending on syngas utilization, it is necessary to improve syngas quality, by different cleaning technologies, as those illustrated in Figure 6.

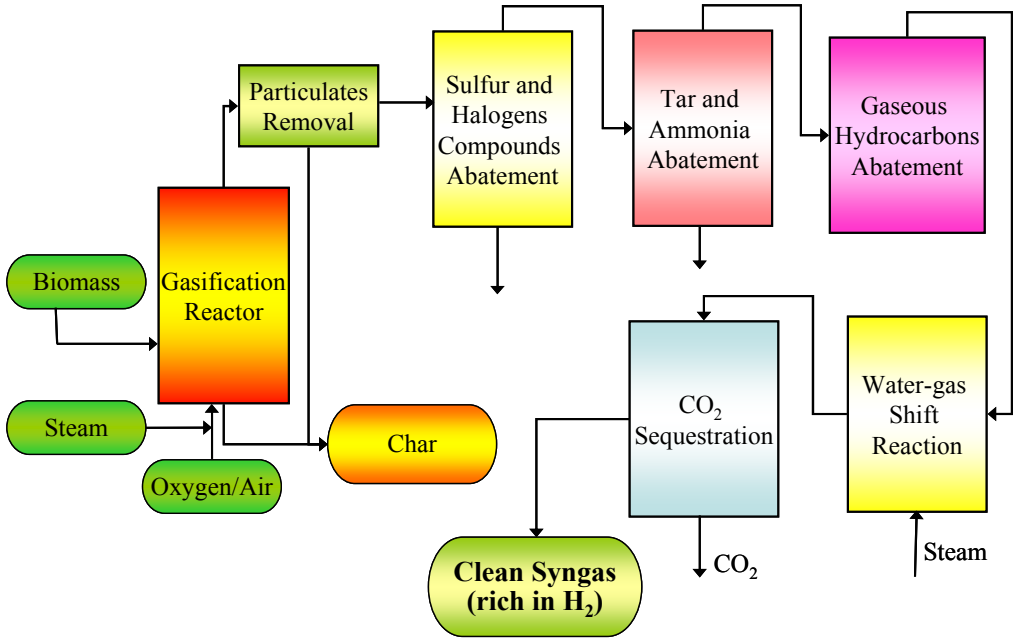

Figure 6. Schematic diagram of the main hot syngas cleaning processes.

6.1. Particulates Removal Technologies

The presence of ash and alkali compounds in syngas may also cause problems of deposition, corrosion and erosion in pipes and in equipment that uses the syngas, such as gas turbines or motors (Gabra et al., 2001). In Table 3 are presented the requirements for different syngas utilizations (adapted from Paarsen, 2006).

Particulate dust and tar may be removed from syngas after gasification by several mechanical methods such as cyclones, bag filters, baffle filters, ceramic filters, fabric filters, rotating particle separators, wet electrostatic precipitators and water scrubbers. However, some of these options present disadvantages. In wet scrubbers, particulates are removed by its collision with liquid sprays, usually water. Water scrubbing and wet electrostatic precipitation produce residual water and apart from the environmental pollution, are economical unattractive Wang et al., 2008.

Fabric filters can remove small diameter particulates and even sub-micron particulates, but the pressure differential across the filter increases as the pore size decreases. They are more useful for removing dry particulates, but less appropriate for wet or sticky contaminants like tar, which are difficult to remove from these materials. Fabric filters and rotating particle separators are not suitable for tar removals. Fabric filters, rotating particle separators and water scrubbers, can only operate at temperatures below 200 ºC, which is inconvenient when syngas needs to be hot cleaned.

For hot gas cleaning processes ceramic filters may be a good option, as they operate at temperature up to a 600 ºC, but as the pressure drop through ceramic filters is high, ceramic filters are usually used for high-pressure gases. Hot gas cleaning processes have the advantages of improving energy efficiency and lowering operational costs when the syngas is

used for hydrogen production through steam reforming and water-gas shift reactions or for heat and power generation in a high-temperature fuel cell. Besides, hot gas cleaning processes have low environmental impact and are normally safe, Wang et al., 2008.

Table 3. Requirements for different syngas utilizations

Impurity	*Boiler*	*Gas Engines*	*Gas Turbines*	*Fuel cells*	*Fischer-Tropsch and methanol Synthesis*
Particulate (mg/Nm^3)	*1 000*	*< 50*	*< 15*	*< 0.1*	*almost completely removed*
Particle size (μm)	*10*	*< 10*	*< 5*	*< 10*	
Total sulfur	*72 mg/Nm^3*	*< 80 mg/Nm^3*		*< 1 ppm*	*< 1 ppmv*
Total chlorine	*35 mg/Nm^3*	*< 100 mg/Nm^3*		*< 1 ppm*	*10 ppbv*
NH_3	*-*	*< 50 mg/Nm^3*		*< 5000 ppm*	*1 ppmv*
Tar (Dew point)	*< 400ºC*	*< 10ºC*		*-*	*not condensing below dew point*
Alkali metals		*0,24 mg/Nm^3*	*0,24 mg/Nm^3*	*< 10 ppm*	*10 ppbv*

The most used devices for particulates removal are cyclones, as they are relatively inexpensive to build and operate, can work over a wide range of temperatures, are commercially available and quite effective at removing particulates with larger particle sizes, above about 5 μm. However, they are inadequate for sub-micron particulates removal and not suitable to retain the vaporized forms of tar and alkali metals.

Gabra et al., 2001a and 2001b studied the effect of using a cyclone to remove particulates and alkali contents from syngas produced by bagasse or cane trash gasification. Though, it was possible to achieve reductions of around 60–70% of the alkali carried out by the syngas, the total alkali and particulates contents of the producer gas were higher than that required by most gas turbines. The syngas produced from cane trash seemed to be a more problematic fuel than bagasse, as some particulates carried over by the syngas have been melted and had K and Na compounds.

Ma et al., 2005 tested a nickel-based catalytic filter material for high temperature removal of tar and particles from biomass gasification syngas. At 850 ºC reductions of 99.0% were achieved, while at 800ºC only 77% tar reductions were obtained. As particles are filtered prior to reaching the catalytic material, they cannot block the catalyst. According, to the authors this filter had a better performance than monoliths, because this later option presented mass transfer problems in the wide channels, which prevented full particle passage. A catalytic filter may be a best option than a filter followed by a catalytic bed or a monolith

followed by a filter, because equipment is simpler and allows taking advantage of the porous filter material for tar conversion.

6.2. Sulfur and Halogens Based Compounds Abatement

Sulfur and halogens contents in biomass affects the release of H_2S and HCl in the syngas, as discussed in § 3. Specific sorbents, containing Fe, Ca and other elements that favor the formation of sulfides and halogenides may be added to the gasification bed to increase sulfur and chlorine retention inside the bed. However, when biomass wastes with high contents of sulfur and chlorine are gasified, it is expected that the release of these elements compounds, even with the addition of specific sorbents, may be high enough to compromise some syngas end-uses. As shown in Table 3, some gas applications require quite low contents of total sulfur and chlorine.

The presence of chlorine and sulfur causes corrosion in turbines, engines, boilers and fuel cells and leads to the formation of SO_x and Cl pollutants in the exhaust gas. The chlorine and sulfur requirements for boilers are based on emission limits, because for these values corrosion in boilers is also minimized. Fuel cells have low chlorine and sulfur requirements, because they cause degradation of the electrodes. Chlorine and sulfur compounds in syngas causes gas engine corrosion and oil degradation. SO_x increase the acidity of the oil and the risk of corrosion and HCl attacks the metal parts of the gas engine and destroys the lubricating oil additives. Both compounds reduce the time between oil exchanges.

The presence of chlorine and sulfur are also disadvantageous when syngas needs to be treated in catalytic processes like tar or hydrocarbons reforming or CO shift reaction to increase H_2 content, because of catalysts deactivation and poisoning by the presence of H_2S or HCl in the product gas. If the gasification gas is going to be used in Fischer-Tropsch synthesis or methanol synthesis, strict sulfur purification processes are required to achieve the low concentrations permitted, otherwise great catalyst damage may occur. Simell et al., 1996 reported that in presence of a Ni-based monolith catalyst to treat syngas at 900°C it was possible to achieve tar and ammonia reductions of 100 and 80%, respectively, however, the catalyst used was susceptible to be poisoned by H_2S and by carbon deposition.

When sulfur and chloride compounds have concentrations higher than those required by gas end-use, gasification gas needs to be treated till the right concentrations are attained. H_2S abatement may be achieved by low temperature methods such as: physical absorption, chemical absorption, oxidation and dry bed processes. However, low temperature methods are not advisable when the gas needs to be further treated by any thermal process, as for instance for tar and hydrocarbons abatement or CO shift reaction. Some natural minerals, like dolomite or olivine are suitable to retain sulfur, chlorine and other halogenides, CaO is the most popular reagent to react with H_2S by reaction (20). CaO and $Ca(OH)_2$ may also react with HCl, through reactions (37) and (38) to form $CaCl_2$, or with HF, HBr and HI by similar reactions. Therefore, natural minerals may be used to treat syngas to further decrease its content in sulfur and chlorine compounds. They are cheap, easy to find and quite effective, the main disadvantage of dolomite is its softness, which makes it easy to break and erode.

Corella et al., 2008 used calcinated limestone (CaO) and calcinated dolomite (CaO . MgO) for hot gas cleaning produced from biomass gasification and found that HCl reacted with the CaO and MgO forming CaCl2 and MgCl2, respectively. As MgO melts at 713ºC and

CaO at 772ºC, at 800ºC the temperature normally used to achieve tar reductions, these compounds particles melt and agglomerate, especially in presence of biomass with high contents of chlorine, which may cause the bed agglomeration and the gasification process to be stopped. To overtake these difficulties the authors suggested to use feedstocks with Cl-content well below 3 wt%, the high value used in this work, or optimize gasification conditions to decrease both the HCl and tar contents in syngas, as with lower tar contents a temperature below 770ºC could be used, thus preventing the collapse of the bed.

The steam reforming Ni catalyst was effective for removal of tar in syngas produced by cedar pyrolysis by Tomishige et al., 2005. However, the catalyst was considerably deactivated in presence of H_2S, though in presence of $Rh/CeO_2/SiO_2$ catalyst, even if the syngas had a high H_2S concentration, no catalyst deactivation was observed. While, the adsorption of sulfur on the Ni catalyst was observed by XPS, the adsorption of sulfur on $Rh/CeO_2/SiO_2$ was below the detection limit of XPS.

6.3. Tar Abatement

Low tar contents in syngas are very important to achieve, because as shown in Table 3, most syngas end-uses for energy generation require low tar contents, the same is also true for chemical synthesis. On of the main problems that still needs to be solved, before biomass gasification could play an important role in energy production is the reduction of high tar contents. Catalytic hot gas cleaning methods are quite promising, because high or even the complete destruction of tar is possible, without creating a waste stream which is difficult to dispose. According to Devi et al., 2005, there are five tar classes, as shown in Table 4. The reduction of all tar classes rise with temperature at around 900ºC in presence of catalysts, occurring complex chemical reactions among different tar classes and gases, which are not well known, thus converting one tar class into another. Devi et al., 2005 stated that thermal treatment even without the addition of any catalysts was enough to remove all the class 2 tar and to solve the solubility problems. Three main groups of catalysts may be used to treat syngas and achieve tar abatement: natural minerals, like dolomite or olivine, metal alkalis such as: KOH, $KHCO_3$ and K_2CO_3 and stable metals such as nickel oxide. Dolomite is the most used natural mineral for tar reduction, because of the low cost, availability and efficiency in catalytic steam and dry reforming of tar by reactions (10), (11), (13) and (14).

Devi et al., 2005 treated the syngas obtained in atmospheric bubbling fluidized bed gasifier in a secondary fixed-bed reactor with a sand bed containing 17% of calcinated dolomite or olivine. Calcinated dolomite led to tar reductions of around 63%, while the presence of olivine only led to tar removals of 46%. Authors attributed the worst olivine performance to low iron content of olivine and also because olivine is not porous, so no internal surface area is available for tar conversion. As other authors have reported higher tar conversions, such as Simell et al., 1996, Devi et al., 2005 attributed the low tar reductions to the relative low amount of catalyst used and expected to improve the conversion of tar by increasing the catalyst amount.

Olivine has a higher attrition resistance, while dolomite is soft, easily erode and break by other solid particles, thus whenever, the tar reduction capacity and activity of olivines and calcinated dolomites are similar, olivines are a better option. Both alkali, olivine and dolomite

catalysts are cheaper, but usually they can not remove all tar in the syngas, so other types of catalysts have been developed and tested.

Table 4. Tar classes and characteristics

Tar Classes	Type of Compounds	Main Problems Caused
1	GC-undetectable tar, heaviest fraction	Condense at very low concentration Responsible for the main condensation problems
2	Heterocyclic compounds with high aqueous solubility	Severe waste water problems
3	Aromatic compounds	No problems Condense only at very high concentrations
4	Light polyaromatic compounds	Remain in large amount even after catalytic treatment at a 900 ºC. Very stable compounds or are formed by breakdown of classes 1 and 5
5	Heavy polyaromatic compounds	Condense at very low concentration Responsible for the main condensation problems

The use of alkali metals, especially potassium in the forms of KOH, $KHCO_3$ and K_2CO_3 reduced significantly tar, increased H_2 and decreased CO in syngas by accelerating water-gas shift reaction, as reported by Wang Lijun et al., 2008. However, alkali metals and salts in biomass can cause plugging and deactivation of other metal catalysts.

Corella et al., 1998 used bubbling fluidized bed to gasify pine sawdust, the gas leaving the gasifier went through a fixed guard bed with calcinated dolomite and then it went to a catalytic bed, where different catalysts from four manufacturers: BASF AG, ICI-Katalco, Haldor Topsøe, and United Catalysts Inc. were tested. The authors reported that this configuration led to an increase in gas yield of $0.2Nm^3/kg$, being the gas richer in H_2 and CO, while CO_2 and hydrocarbons contents decreased.

Several authors have reported that Ni-based and other stable metal catalysts can almost completely remove tar, they are expensive, easily deactivated by coke formation, poisoned by H_2S and sintered by ash melting at high temperature. Therefore, Wang T. et al., 2005a and 2005b developed a combined Ni–dolomite catalyst for steam reforming of tar using metallic nickel as an active phase grafted on dolomite. Wang T. et al., 2005b prepared a modified dolomite by mixing Fe_2O_3 with natural dolomite to increase the iron content for higher activity of tar cracking. Four other catalysts: natural dolomite, modified dolomite, ICI-46-1 and Z409 were tested and compared with Ni-dolomite catalyst. The results obtained with Ni-dolomite at 750 ºC, showed tar reductions of about 97%. Ni-dolomite catalyst is cheaper than other commercially available Ni-based catalysts and showed an admirable activity and anti-coke capacity, since Ni/dolomite ratio was 2.5.

Other authors developed and/or tested Ni-based monoliths. Corella et al., 2004b compared the performance of different catalysts for tar abatement: Ni-based monolith, dolomites and commercial steam-reforming catalysts. The activity of monoliths is similar to that of dolomite. The relatively low performance for tar elimination and the high cost of

dolomites can be compensated by a higher resistance to erosion and longer life. As monoliths can operate with a fuel gas containing particulates, they avoid the use of hot filters. The best performance on tar abatement was achieved with commercial ring steam-reforming catalysts, but they required a hot gas-filtration unit at a temperature of 400 to 550°C, before the catalytic reactor. The problems reported were overtaken and higher tar reductions were achieved by using a two-layer monolithic reactor, which showed to be much better than the former single-layer reactor, allowing reducing tar contents to 150 mg/Nm^3, as reported by Toledo et al., 2006 in a later publication of the same research group. However, the feedstock should have low alkali content (potassium and sodium) to prevent the ash from sticking to the front of the monolith.

Biomass wastes usually have relatively high nitrogen contents, which during gasification generate a syngas with a high NH_3 contents that may change between 500 and 6000 ppmv. During syngas utilization NH_3 is converted into NO_x, whose contents may reach values above the legally accepted limits. Therefore, NH_3 has also to be removed from the syngas. In opposition to dolomite, Ni-based catalysts and other-metal based ones that are effective for tar reduction, has also shown ability for ammonia abatement.

Simell et al., 1996 also reported that a Ni-based monolith was the best option to avoide plugging problems typical for fixed or moving bed reactors, as similar tar conversions were obtained either with this catalyst or with calcinated dolomites and limestones, however, the highest ammonia reductions were also obtained with the monolith type catalyst.

Pfeifer et al., 2008 tested a monolith type catalyst prepared with 3 nickel-based catalysts suitable for complete destruction and reported tar conversion of around 98% and ammonia destruction of about 40% at temperatures from 850 to 900°C. Though, no deactivation was reported, further testing in long-term tests is needed, because deactivation may occur, due to poisoning caused by chemisorptions onto catalyst active sites of impurities such as: sulfur, alkali metals and metals like Fe, As, Zn, Pb, Hg, etc. Catalyst pretreatment with steam and the addition of dopants such as magnesium, calcium, and zirconia proved to be efficient in reducing coke formation.

Catalysts with more than one metal have been prepared for low temperature steam reforming of tar, by combining stable metals such as: ruthenium or nickel bimetallics supported in stable materials like: titania, zironia and carbon, Wang Lijun et al., 2008. Rapagna et al., 2002 prepared and tested tri-metallic and ternary oxide structures catalysts in a fixed bed reactor to reform syngas for two applications: methane reforming with steam and CO_2 and conditioning of the gas produced by biomass steam gasification. $LaNi_{0.3}Fe_{0.7}O_3$ presented the best activity at 800◦C, in presence of hydrogen and with a large excess of steam. CH_4 conversion reached 90%, without leading to any appreciable carbon formation and around 90% by weight of the tar present in the syngas were converted at 800ºC.

6.4. Other Processes for Improving Syngas Properties

Depending on syngas utilization, may be necessary to further decrease hydrocarbons contents. As referred before, some tar abatement catalysts are not appropriate to promote the destruction of some hydrocarbons, especially CH_4. Hence, further hydrocarbons abatement may be needed by catalytic steam reforming processes, which convert hydrocarbons into CO,

CO_2 and H_2 by reactions (8) to (11) and also by reactions (12) to (14), as syngas is usually rich in CO_2.

When the syngas is used in chemical synthesis H_2 and CO contents need to be adjusted till the right ratios are obtained, which depend on the synthesis selected and on the chemical products desired. CO may be converted into H_2 and CO_2 in presence of steam and of a suitable catalyst to promote water-gas shift reaction (7).

Some chemical syntheses also require the strict control of CO_2 contents, thus obliging this gas needs to be removed from the syngas. Several processes for CO_2 capture have been developed to reduce the emission of this greenhouse gas. Pinto et al., 2009 reviewed several processes for CO_2 capture. Conventional processes like chemical stripping, physical adsorption and cryogenics, but all of them have some problems that difficulty its use at large scale. For instance Rectisol and Selexol processes that use physical absorption solvents have low efficiency, mainly due to the great energy consumption and to the need of extensive equipment for solvent circulation and heat exchange. Recent R&D activities have been focused in developing membranes to attain effective CO_2 separation. Though the latest achievements of membrane technologies, the technical and economical suitability of these processes still needs to be demonstrated at large scale.

7. NEW SYNGAS UTILIZATIONS

Syngas produced from biomass gasification can be used in a wide range of applications, which strongly depend on syngas quality and on syngas cleaning technologies. The most known biomass syngas end-use is the generation of heat and power. However, biomass syngas may be also used to produce H_2, synthesize other chemicals and liquid fuels, through Fischer–Tropsch synthesis, synthesis of methanol and dimethyl ether and for the production of bio-based products from syngas fermentation. In Figure 7 are illustrated the most important syngas utilizations.

7.1. Hydrogen Production

After the removal of tar, S, N and halogens compounds by the processes described in §6, hydrogen content of syngas may be increase through the water gas shift reaction (7). The formation of hydrogen may be increased by the use of suitable catalysts. Some Ni-based catalysts have also proven to be adequate to catalyze water gas shift reaction, but has their activity is diminished by sulfur compounds poisoning, it is important to be sure that syngas content on these compounds is low enough. Some water gas shift catalysts have been developed, for instance by CandCS – Catalysts and chemical Specialties with the aim of also converting tar and hydrocarbons and retaining sulfur compounds.

After water gas shift reaction syngas main components are H_2 and CO_2. The later needs to be removed and several different processes may be used, as described by Pinto et al., 2009. These processes include: absorption after contact with solvents, adsorption on activated carbon or other materials, cryogenic separation, and membrane separation. Physical absorption with solvents, though is a well known process, requires large equipment for

solvent circulation and heat exchange, have high degradation rates and have great energy consumption, which leads to low efficiency. CO_2 may be adsorbed in different materials with high surface areas, like activated carbons and zeolites, being the process dependent on temperature, partial pressures, surface forces, and adsorbent pore sizes.

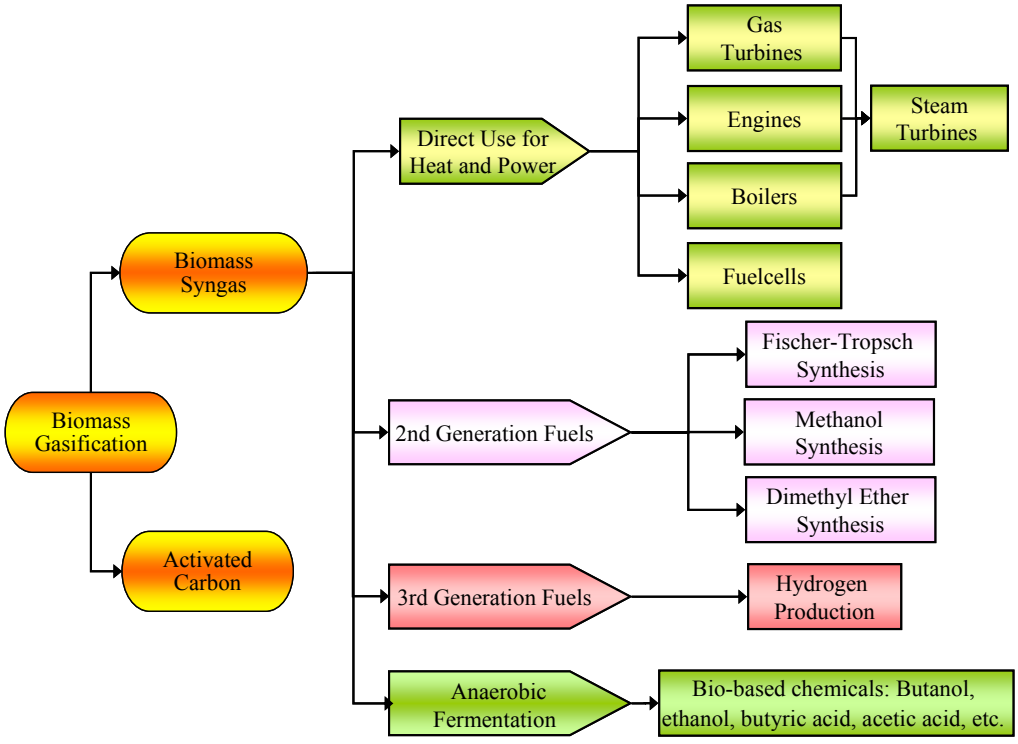

Figure 7. The most important syngas utilizations.

Some technologies are available at commercial scale, but some of them are not suitable for large-scale installations, mainly because the energy needed for regeneration is high, they work at low temperature and their capacity and CO_2 selectivity is low (McKee, 2002).

Hanaoka et al., 2005 proposed a method of integrating in a single reactor steam gasification of biomass, water gas shift reaction and CO_2 absorption using CaO as a CO_2 sorbent, according to reaction (39). CaO played different roles, it catalyzed biomass gasification, retained sulfur and chloride and acted as a CO_2 sorbent.

$$CaO + CO_2 \leftrightarrows CaCO_3 \quad (39)$$

These authors observed that a Ca/C ratio higher than one was enough to absorb CO_2 and H_2 yield and conversion to gas were dependent on the reaction pressure, reaching a maximum value at 0.6 MPa. Though the good results reported, this process was only tested at small-scale and as the CO_2 was released from the $CaCO_3$ by an aqueous solution with HCl, this may bring economical and environmental problems at a large scale installation.

Hydrogen produced through biomass gasification may have a wide range of applications, for energy production it may be used in combustion systems or in fuel cells. Solid oxide fuel

cells are more tolerant to H_2 impurities and can operate with a mixture of H_2 and CO and because of that, their integration with biomass gasifier has been tested.

7.2. Fischer–Tropsch Synthesis

Syngas produced by biomass gasification may be used for Fischer-Tropsch synthesis, but as it usually contains high contents of CH_4 and CO_2, CH_4 needs to be converted to CO and H_2 by steam-reforming, reaction (8). H_2 and CO contents also need to be adjusted till an H_2/CO ratio of 2 is reached, H_2 content in syngas may be increased by water-shift reaction, (7).

Fischer-Tropsch synthesis needs pressures ranging from 20 to 40 bar, temperature from 180 to 250 ºC and the presence of a catalyst, with metals of VIII group of periodic table, like: Co, Ru and Fe. Different types of hydrocarbons (paraffins and olefins) with a wide range of molecular weights and oxygenated compounds like alcohols are obtained, according to reactions (40) to (42).

$$(2n + 1)\ H_2 + n\ CO \leftrightarrows C_nH_{2n+2} + n\ H_2O \quad (40)$$

$$2n\ H_2 + n\ CO \leftrightarrows C_nH_{2n} + n\ H_2O \quad (41)$$

$$2n\ H_2 + n\ CO \leftrightarrows C_nH_{2n+1}\ OH + (n-1)\ H_2O \quad (42)$$

The type of catalyst used affects products selectivity and operating conditions. When a wide range of different types of compounds are formed, Ficher-Tropsch products need to be separated in different fractions and up-graded, before its utilization as fuels.

The economical viability of Fischer Tropsch process could be increased by integrating gas and steam turbines for energy production. The fuel gas from the Fischer Tropsch reactor could be used in a gas turbine for additional electricity production. Streams of the whole process, including the exhaust gas from the gas turbine could be used for superheated steam production to be introduced in a steam turbine to generate electricity. Tijmensen et al., 2002 studied the technical and economical feasibility of biomass integrated gasification–Fischer Tropsch (BIG-FT) processes and they also suggested the use of the combined cycle. The production costs of Ficher-Tropsch fuels are currently higher than those of diesel, however, the use of biomass derived Ficher-Tropsch fuels are promising, as Ficher-Tropsch fuels contain little or no contaminants such as sulfur and aromatics compared with gasoline and diesel (Wang Lijun et al., 2008). On the other hand, with large-scale production, costs are expected to decrease (Tijmensen et al., 2002). Therefore, the main challenge for Fischer Tropsch synthesis are: the development of large-scale pressurized biomass gasification systems, improvement syngas cleaning processes and the development of selective catalysts towards gasoline production at milder temperature and pressure conditions.

7.3. Synthesis of Methanol and Dimethyl Ether

Methanol and dimethyl ether (DME) can be alternatives fuels to gasoline and diesel, as they are clean liquid fuels, without little or no contaminants such as: sulfur, nitrogen or chlorine compounds. Methanol can be synthesized from CO, CO_2 and H_2 by reactions (43)

and (44). The right molar ratios of H_2/CO and CO_2/CO should be used in presence of a suitable Cu-Zn catalyst, at 250 to 300 °C and 5 to 25 MPa.

$$CO + 2H_2 \leftrightarrows CH_3OH \quad (43)$$

$$CO_2 + 3H_2 \leftrightarrows CH3OH + H_2O \quad (44)$$

Methanol also has been used to react with triacylglycerols for the production of biodiesel or after purification may be used to produce gasoline by Mobil Methanol to Gasoline process - MTG, according to reactions (45) to (48). Mobil also developed another process, Mobil Olefin to Gasoline/Distillate – MOGD (Radtke et al., 2006).

$$2\ CH_3OH \leftrightarrows (\ CH_3\ )_2\ O + H_2O \quad (45)$$

$$2\ CH_3OH + (\ CH_3\ )_2\ O \leftrightarrows \text{light olefins} + H_2O \quad (46)$$

$$\text{light olefins} \leftrightarrows \text{heavy olefins} \quad (47)$$

$$\text{heavy olefins} \leftrightarrows \text{aromatics, paraffins, cycloparaffins} \quad (48)$$

Different types of compounds may be formed, which depend on operating conditions and catalysts used, usually zeolites. Hydrocarbons produced, usually present a distillation range similar to those of gasolines and a high octane number, due to its high content of aromatic compounds. While the products obtained by Fischer-Tropsch synthesis usually have higher contents of paraffins and olefins.

Methanol may also be used to synthesize DME through reaction (49) and in presence of a suitable catalyst such as $Cu/ZnO/Al_2O_3+Y\text{-}Al_2O_3$ (Ng et al., 1999) and $Cu/ZnO/Al_2O_3/Cr_2O_3$+ H-ZSM-5 (Tao J.-L. et al., 2001).

$$2CH_3OH \leftrightarrows CH_3OCH_3 + H_2O \quad (49)$$

Ng et al., 1999 reported that by combining the methanol synthesis with the DME production reaction it was possible to increase the overall methanol yield, as by effective removal of the products from the methanol synthesis reaction, it was minimized the reverse reaction. A 2/1 ratio of the commercial $CuO/ZnO/Al_2O_3$ catalyst to the γ-alumina was used. The rise of hydrogen feed concentration enhanced the selectivity to methanol, but decreased that of DME. CO_2 content feed led to strong synergy in total methanol production.

Tao J.-L. et al., 2001 combined the stability of ZSM-5 catalysts with Cu-ZnO-based methanol synthesis catalysts and developed stable hybrid catalyst, $Cu\text{-}ZnO\text{-}Al_2O_3\text{-}Cr_2O_3$ + H-ZSM-5 (SiO_2/Al_2O_3 = 80). The activity of this catalyst was satisfactory, as the total yield of DME and methanol was higher than 26% with over 90% of DME selectivity.

7.4. Production of Bio-Based Products from Syngas Fermentation

Syngas can also be converted into bio-based products including organic acids, alcohols and polyesters by syngas anaerobic fermentation in presence of specific bacteria. In biological

processes, syngas is used as a source of carbon and energy for bacteria growth and biological production of a wide range of products. Several bacteria have been studied and in Table 5 are presented the main biological products obtained.

Worden et al., 1991 stated that the relative proportions of butanol, ethanol, butyric acid and acetic acid could be controlled by adjusting the fermentation pH. Two fermentation processes were developed, one-stage and two-stage. In the single-stage process fermentation conditions to favor alcohol formation were used, while in the two-stage process, conditions to favor the production of butyric and acetic acid were used. These acids were then reduced to the corresponding alcohols by C. acetobutylicum in a second fermentation reactor.

Table 5. Biological products obtained by different bacteria types

Bacteria Type	Products	Main Reference
Butyribacterium Methylotrophicum	Butanol, ethanol, butyric acid and acetic acid	Worden et al., 1991
Clostridial bacteria	Ethanol	Vega et al., 1989 Datar et al., 2004
Photosynthetic bacteria	Poly-3-hydroxybutyrate	Maness et al., 1994
Rhodospirillus rubrum	For H_2 and polyesters	Brown et al., 2003

Biological conversion of syngas has several advantages in relation to chemical processes, because biological processes do not need to operate under high temperature and pressure conditions and the bacterias used in these processes are sulfur tolerant and are not sensitive to CO/H_2 ratio. Hence, expensive syngas cleaning processes are not needed. In addition, product specificity of biocatalysts is higher than that of chemical catalysts. Nevertheless, biological conversion of syngas has some disadvantages in relation to chemical processes, being the main barriers to their commercialization due to difficulties in maintaining anaerobic conditions and mass transfer between gas phase and liquid phase, another difficulty is due to the relatively low rates of bacteria growth and production.

7.5. Production of Heat and Power

Syngas heating value depends on the gasification medium, as stated in §2. Biomass gasification with air usually produces a syngas with low heating value, between 3 and 6 MJ/Nm^3, depending on other experimental conditions, while in presence of steam or oxygen the heating value may increase to values between 10 and 15 MJ/Nm^3. Depending on syngas heating value and content of undesirable compounds like: tar and S, N and Cl compounds it can be used in different devices for heat and power production: combustors, engines and turbines.

Despite the low heating value of syngas, its use in a combustor may have some advantages in relation to biomass combustion, as the percentage of fuel can be increased without any concern about plugging of the feeding system, as it happens during co-firing of biomass and coal. As the temperature of biomass gasification is lower than that of combustion, the problems associated with ash slugging or other ash-related problems can be significantly reduced. Combustors are not so exigent about syngas quality and characteristics,

as are other equipments like turbines or engines, hence the presence of tar and other impurities are permitted in syngas.

On the other hand, if the syngas has a high-quality with almost no tar and dust and high heating value it can be fed directly to gas engines or gas turbines for power generation. Though syngas produced from biomass gasification has a lower heating value than that of natural gas with values around 38 MJ/Nm^3, Sridhar et al., 2001 used the syngas produced from biomass gasification in an engine, which worked smoothly without any sign of knock at a high compression ratio of 17:1 with an overall efficiency of 21% compared to the 31% efficiency in diesel mode. The energy balance showed that about 27% of the energy was lost through the exhaust, about 40% was lost through the cooling water, radiative losses, etc. and 32.5% of the energy was the output power. As the engine combustion chamber had been designed for diesel operation, high energy losses were not surprised, by modifying the combustion chamber, lower energy losses are expected to be obtained.

In gas turbines, the chemical energy of hot syngas is converted into mechanical energy, thus increasing the energy efficiency of conversion and then electricity is produced. The heat of the exhaust gas from the turbine is used to produce steam, which is afterwards used in a steam turbine to produce additional electricity. The steam leaving the steam turbine may be used for heating purposes. By this great energy management, it is possible to increase energy conversion efficiency of the overall process, this is usually done in IGCC installations - Integrated Gasification Combined Cycle that integrate gasification units with gas cleaning processes to allow syngas utilization in gas and steam turbines to produce energy. Energy conversion efficiency is usually around 40 to 45%, but several authors defend that it may be increased up to 55 or 60%, Wang et al., 2008.

There are commercial and demonstration scale installations for power generation in the United States, Europe, and Japan. Each major component of IGCC has been utilized in industrial and power generation applications and some of them have been used to generate electricity from natural gas. IGCC for coal gasification has been demonstrated at a few facilities around the world.

On the other hand, the integration of biomass gasification units with a combined cycle power units to produce electricity in a BIGCC (biomass integrated gasification combined cycle) is relatively new and these processes need further demonstration. In BIGCC may be used combustors, engines and/or gas turbines in different configurations, in Figure 8 is presented one possibility, but several other configurations are also possible. The cleaned hot syngas is introduced in a combustor chamber and the exhausted gases are used in a gas turbine to produce electricity, the gases leaving the gas turbine are used to generate steam, which are used in a steam turbine to produce further electricity. The temperature of the water that leaves the steam turbine may still be high enough to allow some heat recovery.

BIGCC are expected to have significant advantages, namely the increase of energy efficiency and the decrease of environmental impact, due to lower pollutants emissions, water consumption and solid waste production. As, these plants may also incorporate units for capture and storage of carbon dioxide, it is predicted that in the near future, BIGCC installations will be spread all over the world.

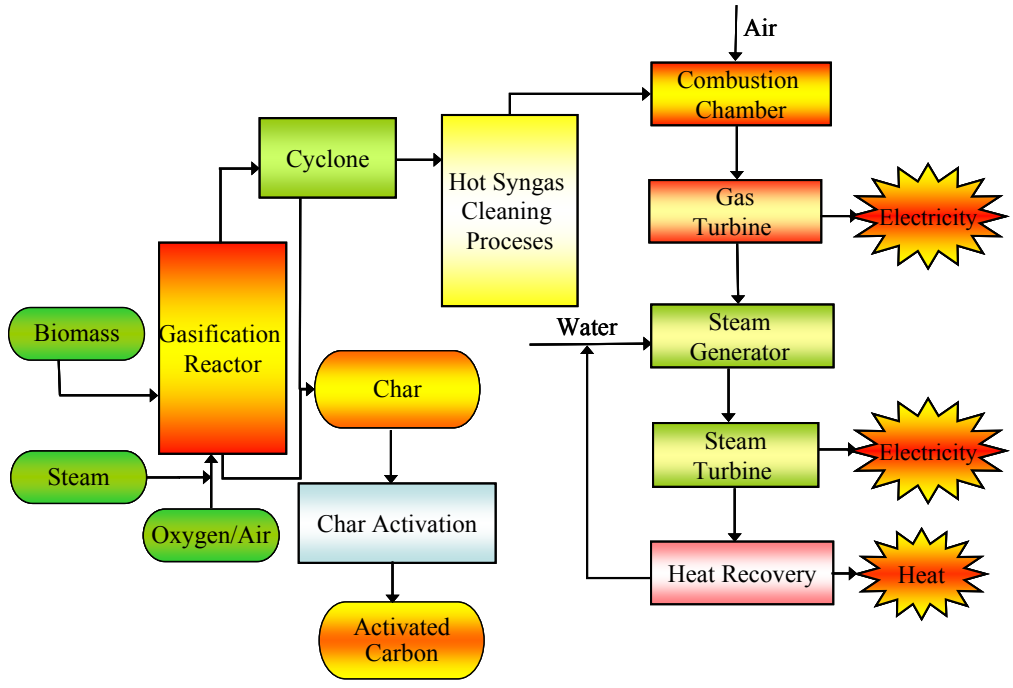

Figure 8. Schematic diagram for one possible configuration for a Biomass Integrated Gasification Combined Cycle (BIGCC).

8. Main Biomass Gasification Barriers and R&D Needs

Biomass gasification technologies can produce heat, power, CHP, and synthesis gas. Biomass may be converted into syngas by fluidised bed gasification or by entrained flow gasification. The second process requires biomass with very small sizes, thus extensive pre-treatment is needed. High gasification temperatures are also required, between 1000 and 1300°C and therefore, the syngas produced usually has little or no methane and other hydrocarbons. Entrained flow gasification processes have been demonstrated at large-scale for coal and some mixtures of coal and biomass with success.

Biomass to be used by fluidised bed gasification processes do not need the extensive pre-treatments mentioned before and lower temperatures are used, around 900°C. However, the syngas produced needs catalytic upgrading to reduce hydrocarbons and tar contents. Biomass fluidised bed gasification technologies for the production of heat and/or electricity have been demonstrated.

In Table 6 are mentioned several biomass gasification technologies which have been demonstrated with success and some of them are now commercial plants. However, before biomass gasification may play an important role in energy generation there is still a long way to run, as there are still several barriers for biomass gasification processes.

The main barriers are the following:

Biomass prices
Flexibility of biomass gasification systems

Gas cleaning research and development (R&D)
High efficiency of integrated gasification combined cycle (IGCC)
Development of synthesis gas conversion processes
Process scale-up and fabrication
Process demonstration

Table 6. Major biomass gasification demonstration projects and commercial plants (www.gastechnology.org/iea)

Country	Biomass Gasification Technology
Austria	8 MWth TUV FICFB BMG CHP demonstration at Güssing 2 MWth down-draft BMG CHP at demonstration at Wr. Neustadt
Belgium	Up to 600 kWe for small-scale power, Xylowatt sa
Canada	50 MWth for synthesis gas/MeOH, Biosyn up to 13 MWth for co-firing, Nexterra
Denmark	5 MWth VØlund up-draft CHP demonstration at HarbØre 70 KWth, Viking 2-stage gasification and power generation at Lyngby 3+MWth, TKEnergi 3-stage, gasification process demonstration at Gjøl (an 833 KWth plant is demonstrated in Japan) 30 MWth Carbona Renugas fluidized bed CHP demonstration at Skive.
Finland	4 to 5 MWth Bioneer up-draft gasifiers (8 in Finland and one in Sweden) 60 MWth, Foster Wheeler Energy CFB co-firing plant at Lahti (50 to 86 MWth co-firing plant in Ruien, Belgium) 40 MWth Foster Wheeler Energy fluidized bed metal recovery gasifier in Varkaus 7 MWth NOVEL Updraft demonstration at Kokemäki 1.8 MWe+3.3 MWth for CHP, NOVEL
Germany	130 MWth commercial waste to methanol plant at Schwarze Pumpe 100 MWth Lurgi CFB gasifier firing cement kiln at Rüdersdorf 0.5 MWth Fraunhofer Umsicht CFB pilot plant at Oberhausen 1.0 MWth CHOREN Carbo-V 2-stage entrained pilot plant in Freiberg 3-5 MWth Future Energy pyrolysis/entrained flow GSP gasifier in Freiberg 75 MWe and MeOH, Future Energy
Italy	15 MWth TPS CFB RDF plant at Greve in Chianti 500 KWth ENEA CFBG pilot plant at Trisaia (similar plant in operation in China).
Netherlands	85 MWth AMER/Essent/Lurgi CFB gasification co-firing plant at Geertruidenberg Biomass co-gasification at the 250 MWe (35 MWe from biomass) Shell entrained coal gasification plat at Willem-Alexander Centrale 3MWth CFBG Plant in Tzum NL Several pilot plants at ECN, Petten ~30% of 250 Mwe, Shell/Buggenum (co-gasification) ~50% of (4x300) Mwe, Shell/Magnum

Table 6. (Continued)

Country	Biomass Gasification Technology
New Zealand	Fluidyne commercial down-draft gasification plants (2 MWe plant in Canada) AB Powerhearth Ltd down-draft BMG (3MWe plant in Maine, USA) 2 MWth Page Macrae updraft BMG plant at Tauranga
Sweden	Bioneer up-draft BMG plant 6 MWe, 9 MWth for CHP, Bioflow 30 MWth Foster Wheeler Energy CFBG at Karlsborg paper mill 20 MWth Foster Wheeler Energy CFBG at Norrsundet paper mill
Country	Biomass Gasification Technology
	30 MWth Gotaverken CFBG at Södracell paper mill 18 MWth Bioflow/Sydkraft/ Foster Wheeler Energy CHP demonstration at Värnamo
Switzerland	200 KWe Pyroforce down draft BMG system at Spiez (scale-up to 1 MWe plant in Austria)
UK	100 KWe Rural Generation downdraft BMG system in Northern Ireland Upto 250 KWe Biomass Engineering Ltd., down draft BMG CHP systems in Northern Ireland Upto 300 KWe Exus Energy down draft BMG CHP systems in Northern Ireland Charlton Energy rotary kiln waste gasification in Gloucestershire Compact Power two-stage waste gasification plant in Bristol
USA	Upto 120 MWth Primenergy gasification/combustion systems (6 in USA and 1 in Italy) Upto 22 KWe Community Power Corporation small modular down-draft gasification systems FERCo SilvaGas dual CFBG Process RENUGAS fluidized bed BMG Process Integrated TCC+Biological Conversion, 11.5million Gals of EtOH/year, Taylor gasification.

Biomass prices are high, mainly due to lack of reliable supply infrastructure, because biomass feedstocks are seasonal and large feed storage capability are needed to control prices. Problems of seasonability could also be overtaken by developing flexible biomass gasification systems that could process a large range of feedstocks, thus enhancing the versatility of biomass gasification processes. However, some of these new feedstocks may contain high levels of sulfur and halogens that may create a very aggressive medium that destroys liners and refractories inside the gasifiers. Some biomass wastes may be more difficult to gasify and may need higher operation temperatures to guarantee the desired level of carbon conversion. Hence, new materials and/or coatings for existing materials are needed to increase the versatility of biomass gasification processes.

R&D for gas cleaning and upgrading is needed to develop low cost and efficient catalysts to accomplish effective abatement of tar, S, N and halogens compounds. The development of multi-function catalyst that may achieve abatement of several types of different compounds would simplify the gas cleaning treatments mentioned before, by eliminating some steps.

Catalyst regeneration is also an important issue, as it may affect technical, economical and environmental viability of all process.

To increase the viability of power generation from IGCC, R&D improvements are needed, especially in the areas of effective carbon capture and sequestration, improvement of existing gasification concepts, advanced cleaning technologies, new gas separation technologies, advanced gas turbines and fuel cells technologies.

Syngas can be used to produce second generation biofuels, such as: Fischer-Tropsch fuels, methanol, ethanol, dimethyl ether and even hydrogen (third generation biofuel). However, extensive syngas cleaning and conditioning is required prior to these syngas conversion processes to produce different fuels and chemicals. The success of these synthesis processes also depend on the development of new catalysts, more specific for the production of desirable products, thus allowing simplifying the processes for products separation. These new catalysts by increasing the efficiency of overall process, will allow improving the technical and economical viability of the synthesis process.

Another barrier is process scale-up, as scale-up by a factor of 10 may be too large and too risky to include guarantees for unproven unit operations, that may be operating with doubtful streams (www.gastechnology.org/iea). Plants with higher capacity usually have higher feedstock costs, as biomass needs to be transported from longer distances. This problem may be overtaken by gasifying biomass at smaller plants near to the geographical existence of biomass and transporting syngas to larger plants where it is converted into biofuels.

It is also important to choose trustworthy engineering and manufacturing companies and use whenever possible, modular shop-fabricated component and units, as they are less expensive than field-fabricated ones, thus allowing optimization of cost reduction.

Process demonstration should last for long periods of time to guarantee good and reliable operation that may validate the process.

The demonstration of most biomass gasification processes has lead to product prices higher than that of conventional products, which means that the commercial success of these processes depend on extra support like adequate incentives and policies and even funding support, through governmental political measures and R&D strategies, supported by research financing programs that may lead to the development of more efficient and cheaper processes.

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Chapter 3

WILLOW BIOMASS GASIFICATION FEASIBILITY STUDY

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ABSTRACT

Willow biomass is found to be an excellent fuel for farm-based power generation by utilizing an advanced gasifier system that uses high-temperature preheated air as the gasification medium. The gasifier's product fuel gas can be used in microturbines to generate electricity or used for other farm energy needs. The gasifier performance under various operating conditions is estimated using a previously developed gasifier model. The net gasification efficiency is about 85 percent under nominal operating conditions. The capital cost of a small, farm-based power system is estimated to be about $2,800/kW. Using the latest published information on willow biomass production cost, the cost of electricity is estimated to be 9 cents/kWh and is reduced to 7.2 cents/kWh when willow is grown on Conservation Reserve land. The costs associated with harvesting, handling, and transporting the willow biomass account for 40 to 50 percent of the annual operating cost. Results also show that co-gasification of willow with low-cost wastes, such as dairy farm animal wastes, can reduce fuel cost, increase the overall fuel availability and help work around problems resulting from seasonal availability of biomass crops. Co-gasification of willow biomass with manure waste also benefits the dairy industry by providing an economical way to dispose of farm wastes and manage nutrient flows.

1. INTRODUCTION

The development of sustainably produced biomass as a feedstock for biofuels, bioproducts and bioenergy is a critical national priority due to concerns about energy security, environment and human health, rural economic development, and the need to diversify products and markets for forestry and agriculture. Biomass for bioproducts and bioenergy can come from a variety of sources including forests, agricultural crops, various residue streams,

and dedicated woody or herbaceous crops. Perlack et al. [1] indicate that perennial woody and herbaceous crops could provide up to 342 million dry tons of biomass annually by 2030, which is about 35 percent of the annual production from agricultural sources. Their development will put more than 20 million ha of land into production, create thousands of rural jobs, and produce an array of environmental benefits. Willow biomass is one of several perennial crops that will contribute to this supply in the Northeast and Midwest regions of the United States [2].

Interest in willow biomass crops has developed over the past few decades because of the multiple environmental and rural development benefits associated with their production and use [1]. Willows have several characteristics that make them an ideal feedstock for bioproducts and bioenergy, including high yields that can be obtained in three or four years on marginal farmland, ease of propagation from dormant hardwood cuttings, a broad underutilized genetic base, ease of breeding for a variety of characteristics, ability to resprout after multiple harvests, and feedstock uniformity.

Applications using willow biomass feedstock for power generation have already been tested at commercial facilities in New York State. Willow biomass has been co-fired with coal in existing utility power plants and direct fired in biomass facilities for production of electricity and/or heat [2]. Co-firing of willow in existing coal power plants resulted in a reduction in SO_x emissions in proportion to the amount of biomass used, and reduced NO_x emissions under certain conditions. While the co-firing of willow works for utility-scale power generation, gasification offers an alternate method of converting willow biomass to energy that would produce substantially less net CO_2 emission, offer more fuel flexibility, and provide opportunities for distributed power generation.

In this chapter we investigate the feasibility of using an advanced gasifier to convert willow biomass crops into a fuel gas that could be used for farm-based power production. In the proposed power system, the gasifier product gas can be used either for generating electricity, using microturbines modified to operate on low-BTU gas, or for other farm energy needs.

An advanced gasifier system, known as MEET (Multi-staged Enthalpy Extraction Technology), was selected for our application. The MEET technology uses high-temperature preheated air as the gasification medium and was originally developed in Japan for converting coal and waste-derived fuels into synthetic fuel gas and value-added byproducts [3]. The MEET gasification system has several attributes, including transportability and fuel-flexibility, which are advantageous for bioenergy applications [4]. One of the objectives of the present study is to investigate the feasibility of capitalizing on these system strengths by integrating a MEET gasifier into the farm operation that includes the production of willow biomass.

Results from our study indicate that willow biomass makes an excellent fuel for the MEET gasifier because of its high heating value, low ash content and high ash-fusion temperatures. The predicted gasification efficiency of the willow-fueled gasifier is about 85 percent. However, higher fuel costs and seasonal variation in availabilities are some of the drawbacks associated with relying solely on willow biomass as the feedstock for energy production. We have also investigated co-gasifying the willow with various amounts of dairy farm animal waste as a way to increase the overall fuel availability and lower the cost of electricity (COE) of this power system. Co-gasifying willow with dairy farm wastes also provides an excellent way to manage nutrient flows on the dairy farm and reduce non-point-

source pollution [5]. Other low-cost agricultural wastes can also be candidates for co-gasification with willow biomass. However, in the present study we have considered only dairy farm waste because of its relative abundance in the upstate New York region.

The MEET process and the components making up the gasification system are described in Section 2. The compositional analysis of the willow biomass and the results of the gasifier performance and economic analyses are described in Section 3. Finally, technology implementation issues and results of the co-gasification study are reported in Section 4.

2. GASIFICATION SYSTEM

The overall scheme of the MEET gasification system is shown in Figure 1. Solid fuel is gasified using preheated air in a reactor vessel to produce a flammable raw synthetic gas. The temperature of the preheated air is typically in the range of 1100 to 1500K. The ash residue from the gasification reactions is extracted from the reactor vessel either as a molten slag (slagging mode of operation) or as ash (non-slagging or dried-bottom operation), depending on the selected operating temperature of the gasifier. Upon exiting the gasifier, the fuel gas is cooled in a heat-recovery boiler and then cleaned using conventional gas cleanup technology. A small fraction of the product fuel gas is diverted to the preheater where it is used for heating the gasification air. Depending on the intended application of the gasification system, the rest of the cleaned fuel gas is utilized for a variety of possible downstream processes.

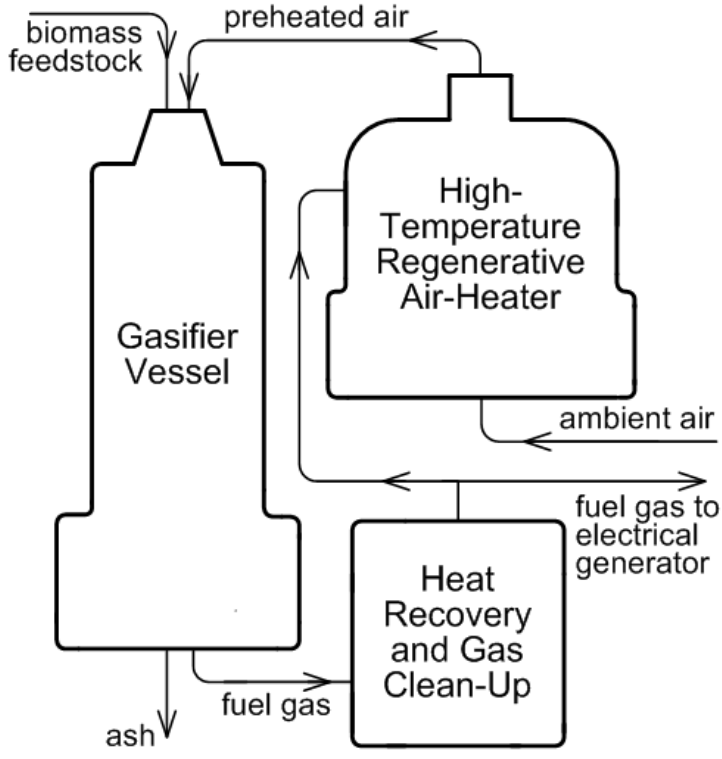

Figure 1. Basic layout of the MEET gasification system.

The gasifier vessel consists of an entrained-flow section, followed by a particulate-removal section. In the slagging MEET gasifier, the gasification temperature is maintained above the fluid temperature (FT) of the ash and a high-temperature ceramic pebble-bed filter is used for slag droplet removal. When the gasifier is configured in the dried-bottom mode, the operating temperature is maintained at a value below the ash's initial deformation temperature (IDT) and an aerodynamic particulate removal device is used for ash rejection. Gasifier operations in the temperature range between the FT and IDT are avoided to prevent ash agglomeration and fouling problems. A compact regenerative heater supplies the high-temperature air for the gasifier [6]. The source of heat for this preheater comes from the combustion of a small amount of the fuel gas produced by the gasifier. The amount of fuel gas needed to fire the preheater depends on the caloric value of the solid fuel, the air preheat temperature and the gasifier operating temperature. For the willow-fueled MEET gasifier, approximately 12 percent by mass of the gasifier product gas is used in the preheater. Most of the energy associated with the fuel gas used in the preheater is recycled through the gasification system in the form of sensible heat of the preheated air and is not lost from the system.

The use of high-temperature air increases the yield of the MEET gasification process over those of conventional air-blown gasifiers [3]. This is because rapid heating of the woody fuel by the high-temperature preheated air greatly enhances the volatile yield from the solid fuel [7]. Also, higher caloric-valued fuel gas can be obtained by using preheated air since the gasifier can now be operated at a substantially more fuel-rich condition to achieve the given gasification temperature.

In addition to higher gasification yields, the MEET gasification system has several other features that are advantageous for biomass power generation applications. These attributes include fuel flexibility, compact size, ability to operate on low-rank solid feedstock and transportability. Additional details of the MEET gasifier technology and current status of its development are described in Pian and Yoshikawa [3, 4].

3. FEEDSTOCK CHARACTERIZATION, PERFORMANCE ANALYSES, AND COST ESTIMATIONS

The compositional and ash properties of the willow biomass feedstock were experimentally determined and the results were subsequently used in our gasifier system performance analyses. Fuel properties and the results of the gasifier performance estimations are summarized in this section. A cost analysis of the willow-fueled farm-based power system is also reported herein.

The State University of New York, College of Environmental Science and Forestry (SUNY-ESF) supplied the willow biomass used in this study. Table 1 shows the ultimate and ash analyses of the willow biomass, which are based on the averages of a large group of SUNY-ESF crops harvested in December 1998. These analyses are similar to those obtained for previous ESF crops [8]. There were only small variations in composition among the different wood samples on a dried basis. However, large variations in moisture content were measured due to differences in harvesting and storage conditions of the test samples. On average, willow biomass has lower fixed carbon and higher volatile matter contents than coal.

It also has a very low ash content. On an energy-per-mass basis, willow is similar to other hardwood species that grow in the northeastern United States.

Table 1. Analyses of the SUNY-ESF Willow Biomass

Ultimate Analysis [a,b]		**Ash Analysis** [b]	
Carbon (wt %)	49.71	Al_2O_3 (wt %)	0.20
Hydrogen	5.97	CaO	41.92
Oxygen	42.16	Fe_2O_3	0.73
Nitrogen	0.50	MgO	3.52
Sulfur	0.03	ZnO	0.35
Ash	1.62	P_2O_5	9.05
		K_2O	13.22
		SiO_2	3.65
HHV (cal/g)	4,798	Na_2O	0.28
		SO_3	2.40

[a] Dried basis. The as-received willow contained approximately 40.5 percent moisture by mass.
[b] Averaged values; based on seven samples of willow harvested and chipped in Dec 1998.

The willow ash's IDT and FT temperatures are important parameters required for configuring the MEET gasifier and for determining its operating condition. The values of these temperatures were determined using a hot-stage microscopic (HSM) technique [9, 10]. Measurements summarized in Figure 2 indicate the values of IDT and FT temperatures are very high, in excess of 1610 and 1700K, respectively. Results also show minimum differences between measurements made in reducing and oxidizing conditions. Temperatures for reducing conditions are typically 10–50K lower than those for oxidizing conditions. This characteristic of the willow ash, which has very low ferric concentrations, is similar to that observed for low-iron coal ash [11].

The gasifier performance under various operating conditions was estimated using a previously developed gasifier model. The model assumes chemical equilibrium conditions and uses the minimization of Gibb's free energy method to determine the thermodynamic properties at the state points. Validation of model results was carried out previously by comparisons with coal-fired gasifier test data [3].

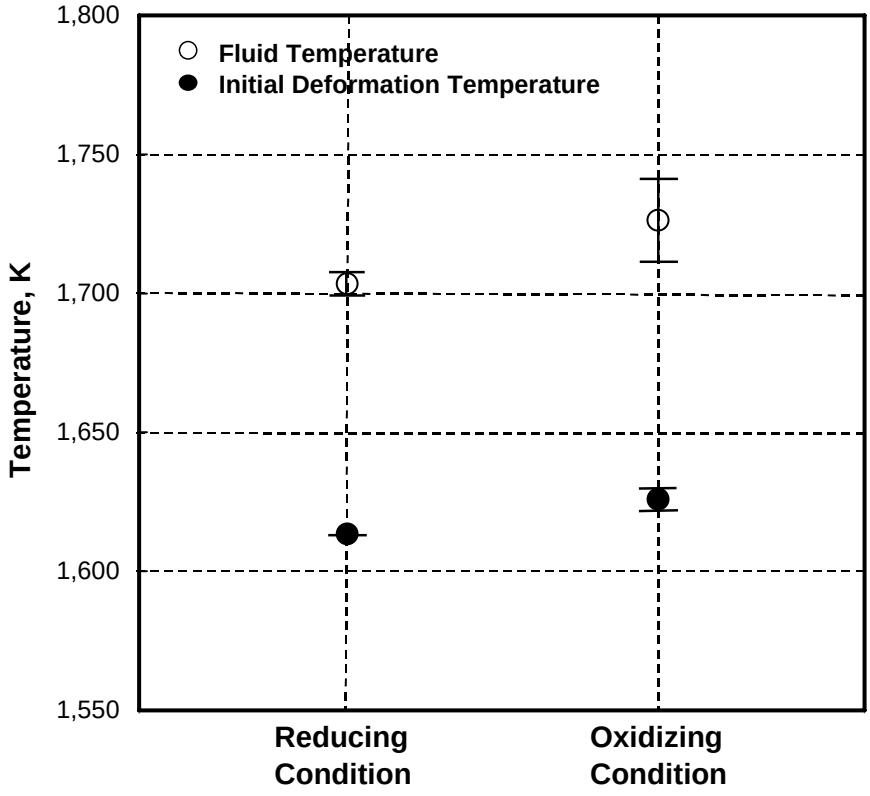

Figure 2. Initial deformation and fluid temperatures of the willow ash under reducing and oxidizing conditions.

Figure 3 shows the configuration of the gasifier subsystem that was used for estimating the efficiency of a non-slagging, willow-fueled MEET gasifier. The operating temperature of the gasifier is 1170K, well below the IDT to minimize ash-fouling problems. The operating temperature is maintained by controlling the fuel/air ratio of the gasifier (equivalent to 26.5% theoretical air). Fuel gas exits the heat-recovery/gas-cleanup system at 650K, suitable for use in a downstream power generation system. Partial heat recovery from the fuel-gas stream is achieved by the integration of a recuperative heat exchanger with wet-type gas cleanup equipment, as described in [12]. The recovered heat can be used for drying the willow-wood feedstock (down to 10% moisture). The exhaust gas from the air preheater, as well as any waste heat recovered from the downstream power generation system, can also be used for drying the biomass feedstock. Enthalpy flux of the various flow streams in Figure 3 is indicated by the number in parentheses, and normalized with respect to the fuel thermal input of 100. As mentioned previously, only a small fraction of the heat energy associated with the fuel gas used to fire the air preheater is lost from the system; most of the energy is recycled through the gasification system in the form of sensible heat of the preheated air.

Gasifier performance was evaluated based on the willow-to-fuel gas conversion efficiency, defined as the higher heating value of the fuel gas divided by the thermal input of the solid fuel. The gross conversion efficiency is determined from the total amount of fuel gas produced by the gasifier. Net conversion efficiency is the gasifier efficiency after subtracting that portion of the fuel gas that is used to fire the air preheater. The gross and net conversion

efficiencies of the gasification system in Figure 3 are 97 and 85%, respectively. The heating value of the fuel gas is 1,600 kcal/m^3 and its composition consists of 31% (molar) carbon monoxide, 6% carbon dioxide, 27% hydrogen, and 36% nitrogen.

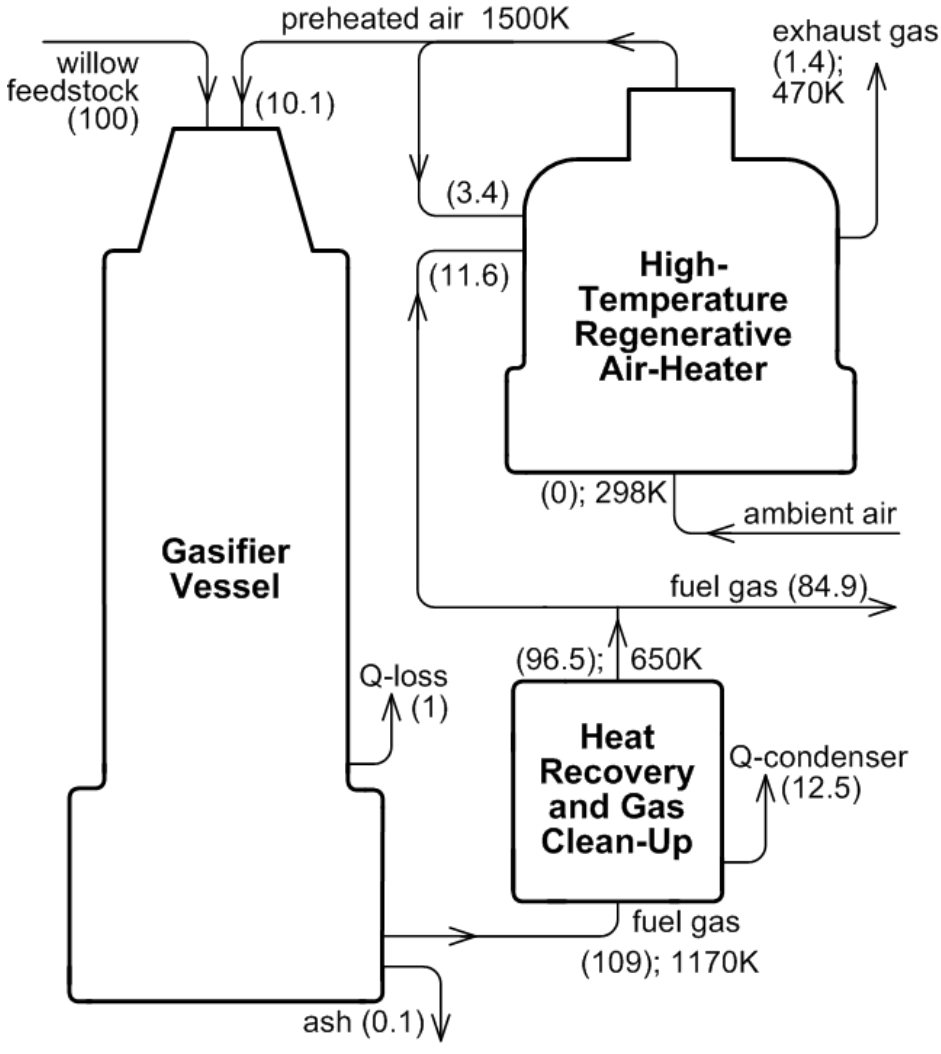

Figure 3. Schematic diagram of the willow-fueled MEET gasification system at the selected reference operating condition.

Figure 4 shows the results of the estimated gasification conversion efficiencies and the heating value of the product fuel gas as a function of the gasification temperature. Operating

the willow-fuel gasifier in the slagging mode would require high operating temperatures, above the ash fluid temperature of 1725K. The gasifier conversion efficiencies and caloric value of the product gases are reduced at such high gasification temperatures. For this reason, we anticipate operating the willow-fueled gasifier in the non-slagging mode, i.e., gasification temperature in the range of 1070 to 1170K. Although the model predicts even better gasifier performances at lower operating temperatures, in actual practice the gasification efficiencies decrease at temperatures less than ~1070K due to tar formation and incomplete carbon burn out.

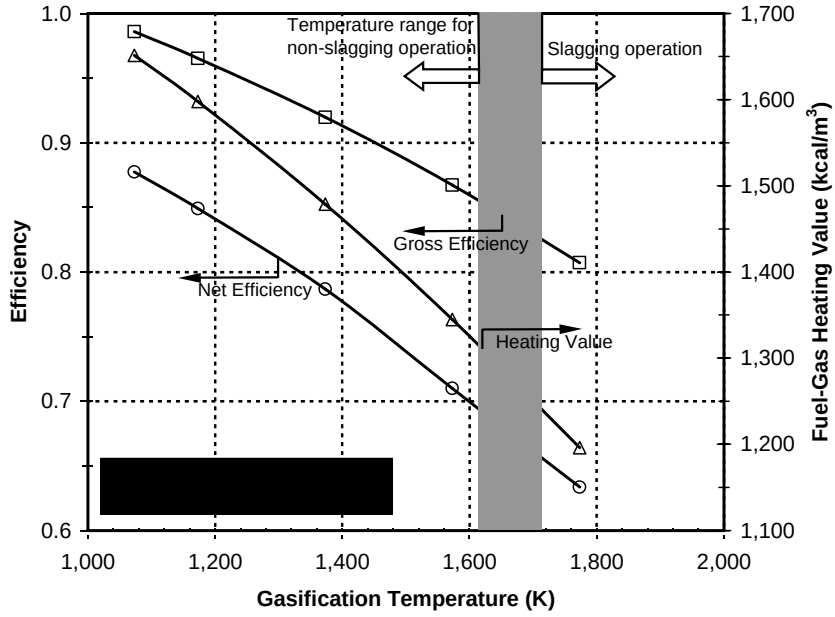

Figure 4. Gasification efficiencies and heating value of fuel gas vs. gasification temperature.

Figure 5 shows the sensitivity of the MEET gasifier performance to air-preheat temperature, at the nominal condition of 1170K operating temperature and 10 percent fuel moisture. For comparison, the performance of a conventional gasifier (298K air temperature) is also shown in the figure. One can achieve a much more fuel-rich condition in the reactor vessel (equivalent to 26.5% theoretical air) with 1500K preheated air than with ambient-temperature air. The conventional gasifier's efficiency and the heating value of the fuel gas are both lower, being 82.6% and 1,187 kcal/m^3, respectively. The fuel gas composition of the conventional gasifier consists of 23% (molar) carbon monoxide, 9.6% carbon dioxide, 19.5% hydrogen, and 47.7% nitrogen. Although results in Figure 5 show even higher gasifier efficiencies at air preheats greater than 1500K, the maximum temperature achievable with the current MEET preheater design is 1500K at the flow rates required for our gasifier application.

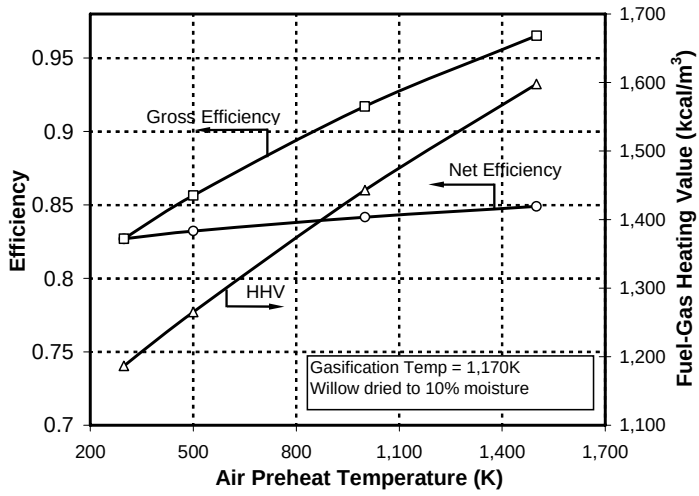

Figure 5. Gasifier efficiencies and heating value of fuel gas vs. air-preheat temperature.

For the cost analysis, we selected a MEET system with a capacity for processing approximately 160 kg of dried willow biomass per hour. For a gasifier of this scale, one reactor vessel can process the yearly crop yield of a 106-ha farm. For larger sized farms, multiple reactor units will be used. A MEET gasifier of this size has been previously built and tested by Pian and Yoshikawa [3]. This refractory-lined vessel, with exterior dimensions of approximately 1-m diameter and 3-m length, can be mounted on a flatbed truck for mobile applications.

Microturbines, modified to operate on low-calorific fuel gas, will be used to generate electrical power for our small on-farm applications. FlexEnergy developed these 30-kW units in partnership with Capstone Turbine Company. Fuel gas-to-electricity conversion efficiencies of the order of 22% have been achieved during initial demonstration tests using low-caloric fuel gas [13]. If one assumes all the fuel gas available from the gasification of willow from 106 ha of farmland is to be used to generate electricity, then five microturbine units are required to support each gasifier unit.

A willow production cost of $49.6 per metric ton of dried willow wood chips (delivered price at the plant gate) was used in our cost analysis. The willow production cost was determined from actual field experiences accumulated by SUNY-ESF [14]. The delivered price is reduced to $31.7 per metric ton of dry wood if the landowners received cost-share payments for the establishment of willow crops and annual rental payments similar to those offered under the USDA's Conservation Reserve Program (CRP). Based on a power production system for a 106-ha farm, consisting of a MEET gasifier and five microturbines, the capital cost is estimated to be about $2,833/kW. The COE is estimated to be $0.09/kWh assuming a 25-year lifespan for the capital equipment, an annual 6% interest rate, and an averaged availability of 85%. The COE includes an operation and maintenance cost of $0.012/kWh. The value of COE would decrease to $0.072/kWh if CRP's contributions are included as part of the cost calculation. Possible economic benefits from the sale of process

heat, recovered solids, or other "green energy" price premiums and tax incentives were not factored into our cost analysis.

4. FEASIBILITY AND IMPLEMENTATION ISSUES

The calculated performances of the gasifier and the estimated COEs were used to assess the commercial feasibility of the willow-fueled gasification power system. Since the gasification technology can be applied to many segments of the power industry, from centralized utility power generation down to small distributed-power applications, the commercialization paths will be different for the different intended applications. We have concentrated on small, farm-based power generation applications.

The commercial viability of willow as a bioenergy fuel will be strongly influenced by the overall system economics, i.e., it must be able to compete in a market where there is already an abundance of low-cost and negative-cost waste fuels. Being a cultivated crop, willow biomass is still a relatively expensive fuel. As with any biomass energy system, the main cost drivers are associated with the harvesting, handling, and transporting of the biomass fuel [14]. In the willow power production system, the fuel cost accounts for 40 to 50 percent of the annual operating costs. For this reason, continuous efforts have been made to reduce the cost of willow biomass crops by optimizing the willow crop production system and adding value to the multiple environmental and rural development benefits associated with the crop, including CRP's, biomass tax credits, green pricing premiums, and agricultural tax assessments on land used for growing willow crops.

Another issue with the willow fuel is its seasonal availability. Willow biomass crops are typically harvested in late fall and during the winter. Storage and scheduling of fuel will be needed in order to use willow for year-round power generation. One way to increase the overall fuel availability, to ease the effects of seasonal variability of willow supply, and possibly to lower the COE of the power system is to co-gasify willow along with agricultural or other wastes that might be available nearby. The MEET gasifier, with its flex-fuel capability, is well suited for such co-gasification applications.

Dairy farm animal waste is a good choice for our co-gasification fuel. A major problem facing the dairy industry is the proper disposal/utilization of livestock waste. Dairy farms have historically imported three times more nutrients than they export [15]. Field spreading of manure, to recycle the nutrients to the crop fields, can cause soil to become saturated resulting in non-point-source pollution. As stricter environmental regulations are applied, farms need a way to reduce the amount of manure they need to spread in a cost effective manner. Gasification offers an economical way to dispose of the wastes and to remove the nutrients from the farm. The power generated from the animal waste can be used on the farm or sold to offset the cost of waste treatment.

Preliminary analyses are carried out to help evaluate the effect of co-gasification on gasifier performance and COE, as well as to identify possible benefits for the dairy farm operators. In the proposed scheme, shown in Figure 6, chipped willow will be made available to the dairy farm for use as animal bedding. In exchange, the liquid portion of the animal manure will be transported to the willow farm for use as fertilizer. The solid portion of the manure and the soiled bedding from the dairy farm are used to augment the willow biomass

fuel for the gasifier. The nutrients, concentrated in the gasifier's bottom ash, can easily be transported off the farms and used as fertilizers. The export of nutrient from the dairy farm, in the form of liquid manure to the willow fields and solid manure to the gasifier/power system, will help reduce or eliminate field spreading of manure, which currently cost dairy farms an averaged of about $50/cow/year in labor and equipment [15]. The proposed arrangement will also eliminate the need for dairy farms to purchase wood chips and sawdust for beddings, resulting in a saving of approximately $50–100/animal/year [16]. In order for this scheme to be feasible, the willow production fields will need to be in close proximity to the dairy farms to minimize transportation costs, or they can be strategically located on the dairy farms and integrated directly into the dairy farm operations.

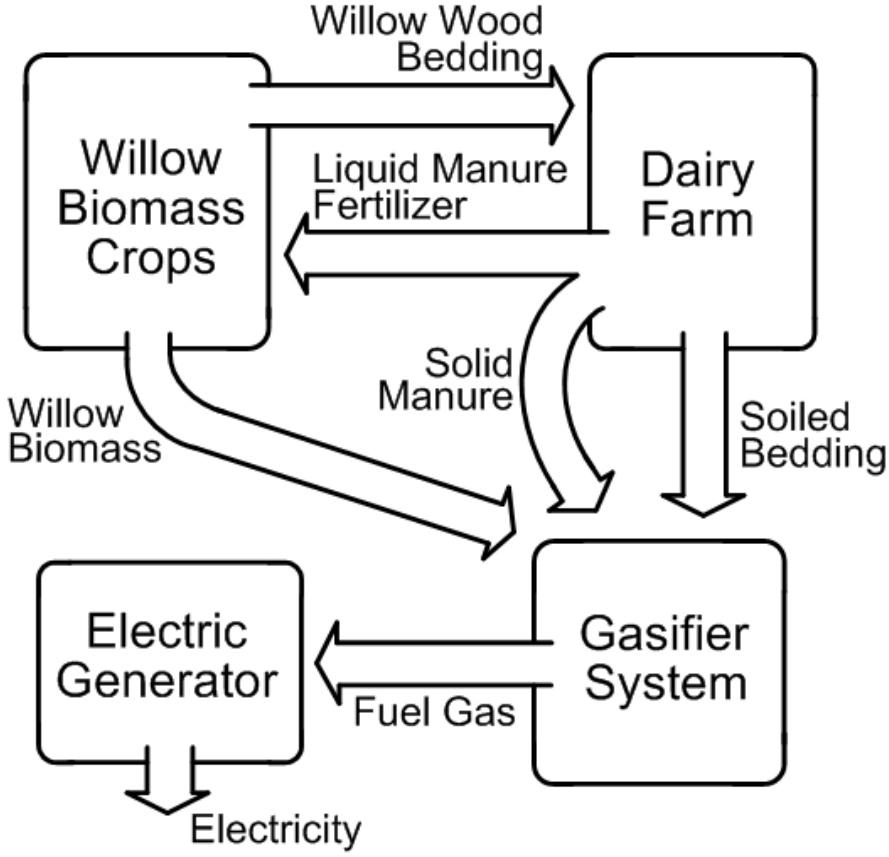

Figure 6. Proposed farm-based power system for co-gasification of willow biomass and dairy farm wastes.

The manure properties used in the co-gasification analyses were taken from an earlier manure-waste gasification study [5]. The ultimate and ash analyses of the manure waste are similar to those for grass and hay, except for higher ash and SiO_2 contents, which presumably are caused by the soil that was picked up during manure collection or ingested by the cow while feeding. The ash-fusion temperatures of the willow-manure fuel mixes were again determined from hot-stage microscopic measurements. Results of the IDT and FT temperatures of the willow/manure ash are shown in Figure 7 for varying mass fractions of

willow biomass in the overall gasifier feedstock. The ash-fusion temperatures of the fuel decrease with increasing fractions of manure. This trend is due to the higher concentrations of phosphorus, potassium and sodium in the manure ash, which act as fluxing agents, as well as higher concentration of SiO_2, which can form an eutectic with the CaO that lowers the fusion temperatures. Comparison of ash-fusion temperature measurements made in reducing and oxidizing conditions also showed minimum differences between the values. Based on these HSM results one can conclude that operating the MEET gasifier at 1170K should not encounter any ash fouling problems for any mixture ratios of willow and manure.

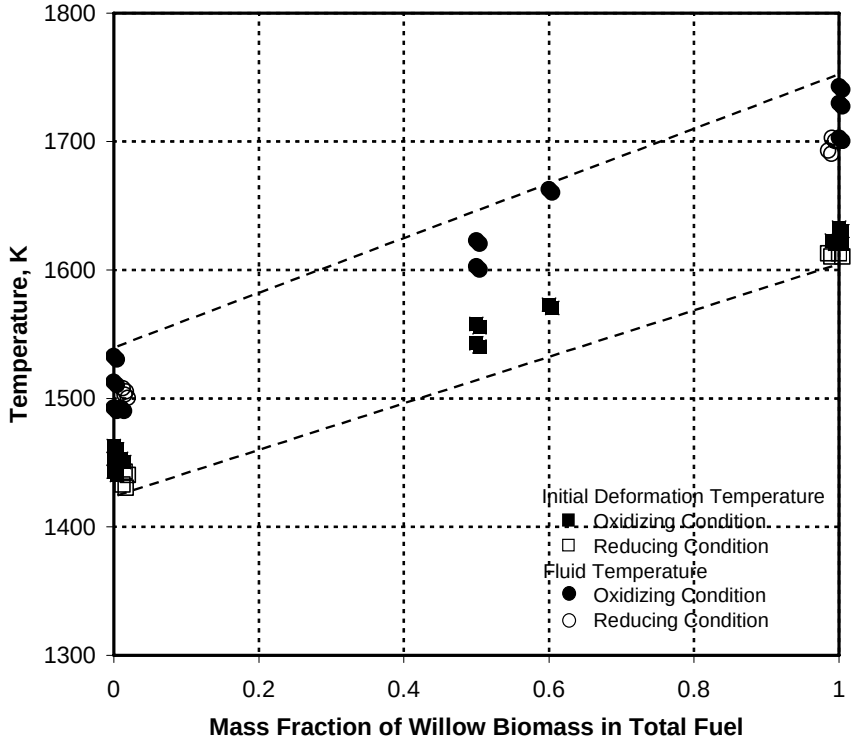

Figure 7. Ash-fusion temperatures, determined from hot-stage microscope data, for fuels consisting of different ratios of willow biomass and dairy farm wastes.

Figure 8 shows the estimated net gasification efficiencies and COE for the co-gasification of willow with various amounts of manure wastes. Gasification temperature of 1170K, air-preheat temperature of 1500K, and fuel moisture content of 10% are assumed in the performance analysis. The gasifier efficiency decreases with increasing mass fraction of manure waste in the total fuel. This behavior can be attributed to several factors. The heating value of the manure waste is approximately 10% lower than that of the willow biomass. Consequently, as the mass fraction of manure waste increases, the gasifier operates at a less fuel-rich condition and larger fractions of the incoming fuel is used to maintain the gasification temperature at 1170K, resulting in a lower caloric-valued product gas. With increasing manure mass fraction, greater amount of the product fuel gas is used in the air preheater, also contributing to lowering the net gasifier efficiency.

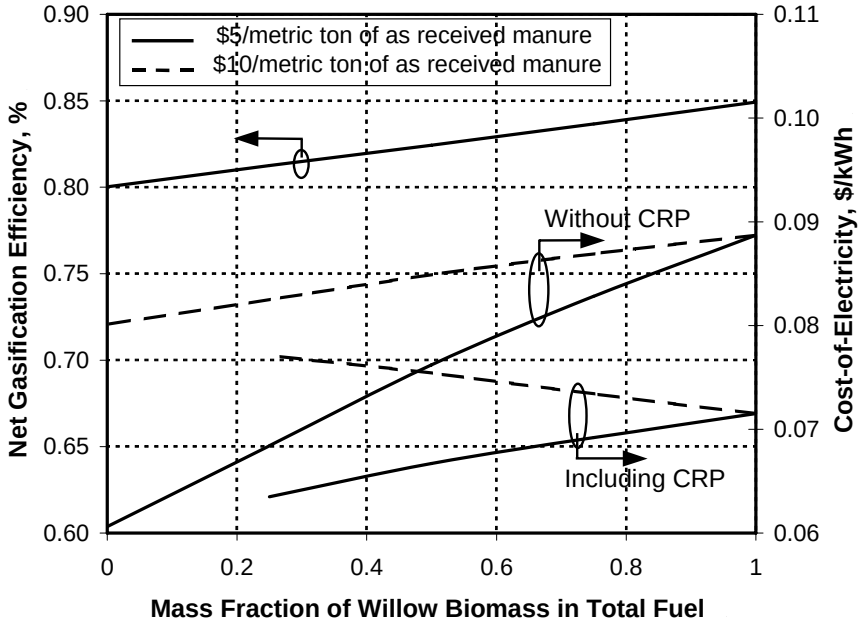

Figure 8. Net efficiency of gasifier and cost-of-electricity vs. mass fraction of willow in fuel mixture.

Figure 8 also shows the sensitivity of COE to different fuel-cost scenarios. Estimated COE's are shown for willow costs with and without CPR contributions, and for two manure-waste costs to account for various farm-specific factors such as manure preparation, handling, and transportation. For three of the scenarios the addition of manure to the gasifier fuel decreases the cost of power. The exception is when willow is grown on CPR land and the manure costs $10 per metric ton. In that case the cost of power is lowest when the gasifier fuel is 100 percent willow biomass, although the differences are small. The opportunity to economically manage manure with this system is probably more valuable then the slightly cheaper power using no manure waste. In general, the ability of co-gasification to lower COE increases with increased availability of low-cost wastes. Also, co-gasification can be a viable method to keep the willow-gasification power system commercially competitive after the various tax incentives, such as CPR, have expired.

Usage of willow as bedding for dairy cows shows no evidence of being very different then any other wood bedding, assuming similar wood particle size and moisture content. However, dairy operators are reluctant to switch to willow for bedding in place of their current practice unless they can be convinced the practice is safe and beneficial to them. The willow must be proved acceptable by demonstration of use and the cost must be shown to be substantially lower than the current wood-bedding cost of $50/cow/year. Several New York-based dairy farms have agreed to participate in trial demonstration tests, using willow bedding in heifer pens. Initial test results indicated the willow would need to be chipped finer, to the consistency of sawdust, and dried to a moisture content of between 20 to 45%. Both requirements can be met using existing harvesting machines and the MEET gasification system. The chipped willow's particle size can be changed by new forage-harvester-based systems that are being developed for willow biomass crops. Lower moisture content is obtainable by using the waste heat of the power system to dry the willow or by letting the

willow sit on the field/storage for longer period of time prior to their use. The benefits to the dairy farms are numerous. In addition to lower cost for bedding, and environmental and financial benefits from better nutrient management, the energy produced from the manure waste can contribute to lower farm operating cost; and in many cases become another source of revenue for the farms. In an earlier manure-gasification case study, we have found that the production of fuel gas from gasification of farm animal waste from a particular upstate NY dairy farm can produce almost four times the amount of energy necessary for energy self-sufficiency [5].

For small-scaled farm-based power generation applications, we anticipate new business opportunities will arise for private companies to manage and operate the gasification systems. If a farm is large enough, a gasifier could be located on the farm itself. To service smaller farms, the gasifier could be centrally located and operated by a company to process willow collected from a number of farms. The fuel gas could be used either on site, or piped away for use in a power plant. There are several other reasons why a separate company would be required to provide the gasification service. Firstly, willow growers are generally not interested, nor do they have the time and resources, to own and operate this type of equipment. Their preference is to sell the wood as a commodity to the operating company. Secondly, from a business point of view, it is far better to take advantage of the flex-fuel capability of the MEET gasifier, operating it not only on willow, but using whatever wastes are available in order to maintain low fuel costs and high operational availability. Unlike a farm-owned gasification business, an independent operating company will be able to take advantage of this flexibility. Although it is beyond the scope of this investigation to include the results of waste studies other than co-gasification with dairy farm waste, it is suffice to say that the flexibility of the gasification system would allow the inclusion of many waste forms, some with negative costs such as landfill yard waste. Additionally, the operating company could potentially charge a "tipping" fee for accepting the waste streams.

5. CONCLUSION

Willow biomass makes an excellent fuel for the advanced MEET gasifier because of its low ash content, high heating value and high ash-fusion temperatures. The predicted net gasification efficiency of a willow-fueled MEET gasifier is about 85 percent. The fuel gas can be used to operate microturbines for a farm-based power generation system. The capital cost for this power system, suitable for a 106-ha sized farm, is estimated to be about $2,800/kW. Using the latest published information on willow biomass production cost, the COE is estimated to be 9 cents per kWh. When the contributions from the Conservation Reserve Program are included as part of producing the willow biomass, the COE is reduced to 7.2 cents per kWh.

One way to lower the COE of the power system, as well as to ease the effects of seasonal variability of willow supply, is to co-gasify willow along with agricultural or other wastes that might be available nearby. We have investigated the feasibility of co-gasifying willow biomass with various amounts of dairy farm livestock waste. A farm-based power system based on co-gasification also benefits the dairy farm operators by offering an economical way to dispose of the wastes and to remove the nutrients from the farm. The power generated from

the animal waste can be used on the farm or sold to offset the cost of waste treatment. In order for this scheme to be feasible, the willow production fields will need to be in close proximity to the dairy farms to minimize transportation costs, or they can be located on the dairy farms and integrated directly into the dairy farm operations.

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Chapter 4

BIOWASTES-TO-BIOFUELS ROUTES VIA GASIFICATION

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ABSTRACT

Nowadays, biomass has a well-known potential for producing energy carriers, such as electricity, heat (steam) and transport biofuels. However, biomass availability is rather limited and stochastically distributed. This could be a major problem in demographically dense regions where land is scarce and biomass may compete with other applications, notably agriculture for food production. In fact, this is the case for the first-generation biofuels (e.g. bioethanol and biodiesel) that are mainly produced from biochemical conversion of food crops such as sugar cane, corn or wheat, and vegetable oils from feedstock like rapeseed or palm oil. Moreover, when taking into account emissions from transport and conversion treatments, life-cycle analyses reveal that first-generation biofuels frequently exceed the emission thresholds of fossil fuels.

Second generation biofuels are now being developed as a possible better alternative to the first generation, as they can use non-food crops (e.g. switch grass) or biowastes from different origins (e.g., forest, agriculture, industry, municipalities). Second generation biofuels can also be produced via either biochemical or thermochemical conversion. Among all the existing thermochemical conversion technologies, gasification is gaining interest due to its higher efficiency, larger scales, and reliable operation.

However, biowastes-to-biofuels conversion involves several challenges. Firstly, the existing technology must be re-designed and optimized to become cost and efficiency competitive with fossil fuels. Moreover, due to the wide diversity of biowastes and biofuels that can be obtained, the most sustainable conversion routes must be properly selected. Hence, an inherent challenge is to develop a reliable model to evaluate the sustainability of any process.

In this chapter we present the evaluation of second generation biofuels (SNG, methanol, Fischer-Tropsch fuels, hydrogen) as well as heat and electricity, from different biowastes via gasification with subsequent catalytic conversion of syngas. Pre-treatment steps are also considered in order to enhance the low energy density of biomass prior to

gasification. However, since pre-treatment is directly affected by local conditions, the Dutch province of Friesland is taken as a case study. The biowaste-to-biofuels routes are modeled in Aspen Plus, and mass and energy balances obtained from simulations are later used for efficiency evaluation. Results are presented in terms of mass conversion yield, energy and exergetic efficiency. The last part of the paper is devoted to explain how those results will be integrated for combined economic and environmental impact analysis.

NOMENCLATURE

c: kinetic energy of a stream (kJ/kg)
C_p: specific heat capacity (J/mol.K)
C_S: calorific value of biomass (J/mol)
Δg_{mix}: Gibbs energy of mixing (MW)
ΔH_{298K}= enthalpy or reaction (kJ/mol)
$E_{biofuel}$: total exergy of a biofuel stream (MW)
$E_{biomass}$: total exergy of a biomass stream (MW)
$E_{H2O,liq}$: total exergy of liquid water (MW)
E_{NG}: total exergy of natural gas (MW)
E_{input}: total exergy required for a process (MW)
E_{output}: total exergy obtained from a process (MW)
$E_{surplus\ steam}$: total exergy of surplus steam (MW)
$E_{utilities}$: total exergy of utilities (MW)
E^Q: total exergy of a heat flow (MW)
g: gravity (m/s^2)
H/C, O/C, N/C: atomic ratios in the biomass
h: enthalpy of a stream (kJ/kg)
HHV: high heating value (kJ/kg)
I: Irreversibilities (exergy losses) (MW)
I_N: Intensity (Ampere)
k_{HC1}: rate constant for adsorption of CO on an active site (mol/g.s.bar)
k_{HC5}: rate constant for desorption of paraffins by hydrogenation of active site (mol/g.s.bar)
k_{HC6}: rate constant for desorption of olefins from active site (mol/g.s)
L: length of the conveyors (in ft)
$LHV_{biomass}$: lower heating value of biomass (kJ/kg)
$m_{i,\ inlet}$: mass flow rate of an inlet compound i (kg/s)
$m_{j,outlet}$: mass flow rate of an outlet compound j (kg/s)
n_i: molar flow rate of a compound i (kmol/s)
n_{tot}: total molar flow rate of a stream (kmol/s)
P: pressure (bar)
P_o: reference pressure (1 bar)
P_{CO}: partial pressure of CO (bar)
P_{H2}: Partial pressure of H_2 (bar)
Q: heat flow (MW)

R: universal gas constant (8.314472 J/mol.K)
R*: reduction ratio of the sizing equipments (-)
T: temperature (K)
T_o: reference temperature (298.15 K)
W_i: Wobbe index (MJ/Nm^3)
W_{in}: work input for a process (MW)
W_{out}: work output from a process (MW)
W_n: mass fraction of a product with n C atoms (%)
x_i: molar fraction of compound i (%)
z: potential energy of a stream (kJ/kg)
z_i: mass fraction of compound i (%)
z_{org}: organic mass fraction of biomass (%)

Greek symbols

α: chain growth factor probability **(-)**
β: ratio of the chemical exergy to the LHV of the organic fraction of biomass (dimensionless)
$\varepsilon_{ch,biowaste}$: specific chemical exergy of biowaste (J/mol)
$\varepsilon_{ch,i}$: specific chemical exergy of compound i (J/mol)
$\varepsilon_{ph,i}$: specific physical exergy of compound i (J/mol)
η_{HHV}: efficiency based on HHV of biowastes and biofuels
η_{LHV}: efficiency based on LHV of biowastes and biofuels
κ: reaction conversion (%)
μ: mass conversion yield (kg biofuel/kg biomass)
ρ_{air}: density of air (kg/m3)
ρ_g: density of gases (kg/m3)
Ψ_{HHV}: overall HHV efficiency (%)
Ψ_{LHV}: overall HHV efficiency (%)
$\Psi_{\varepsilon ch}$: chemical exergetic efficiency (%)
Ψ_{ex}: total exergetic efficiency (%)

Acronyms

ASU: Air Separation Unit
BEV: Battery Electric Vehicle
BFB: Bubbling Fluidized Bed
BIGCC: Biomass Integrated Gasification Combined Cycle
CExC: Cumulative Exergy Counting
CFB: Circulating Fluidized Bed
CHP: Combined Heat Power production
CNG: Compressed Natural Gas
COS: Carbonyl sulfide

DC: Direct Current
DME: Dimethyl ether
DMFC: Direct Methanol Fuel Cell
DSS: Decision Support System
EEA: Extended Exergy Accounting
EI: Eco-Indicator
ELCA: Exergetic Life Cycle Analysis
ER: equivalence ratio of air
FCV: Fuel Cell Vehicle
FFV: Flexible-fuel vehicle
GHG's: greenhouse gases
HRSG: Heat Recovery Steam Generation
HTS: High Temperature Shift reactor
HTU: Hydrothermal Upgrading
ICE: Internal Combustion Engine vehicle
ICE-CC: internal combustion engine combined cycle
IGCC: Integrated Gasification Combined Cycle
ITSOFC: Intermediate Temperature Solid Oxide Fuel Cells
KEMDEA: electrolytes packages from the Aspen Plus library
LCA: Life Cycle Analysis
LCC: Life Cycle Cost analysis
LCIA: Life Cycle Impact Analysis
LPG: Liquefied Petroleum Gas
LTS: Low Temperature Shift reactor
MC: moisture content (%)
MCFC: Molten-Carbonate Fuel Cell
MDEA: N-methyl-diethanolamine $C_{12}H_{17}NO_2$
MSW: Municipal Solid Waste
MTBE: Methyl tert-butyl ether
PAH: polyaromatic hydrocarbons
PBI: Polybenzimidazole fiber
PEM: Proton Exchange Membrane (fuel cell)
PSA: Pressure Swing Absorption system
RADFRAC: rigorous phase fractioning column model from the library of Aspen Plus
REQUIL: equilibrium reactor model from the library of Aspen Plus
RDF: Refused Derived Fuel (waste)
RGIBBS: Gibbs energy minimization reactor model from the library of Aspen Plus
RSTOIC: stoichiometric reactor model from the library of Aspen Plus
RYIELD: yield reactor model from the library of Aspen Plus
SMR: Steam Methane Reforming process
SNG: Synthetic Natural Gas
SOFC: Solid Oxide Fuel Cell
SRF: Short Rotation Forest
TE: Thermo-Economics analysis
TOC: Total Operational Cost
TSOFC: Tubular Solid Oxide Fuel Cell

WGS: Water-Gas Shift
WTW: Well-to-Wheel analysis

1. INTRODUCTION

1.1. Current Scenario

Existing environmental and economical problems, such as global warming, ozone layer depletion, dependence on petroleum nations and future depletion of fossil fuels, prompt governments to search for urgent solutions.

This is of crucial importance for a society with limited natural sources but an explosive rate of human population growth and living standards. In the last 20th century, the world human population has increased from 1.65 billion to almost 6 billion in 1999 and it is projected to reach 8.9 billion by 2050. This growth has been accompanied with a significant increase of fossil fuels consumption, i.e., from 299 EJ in 1980 to 509 EJ in 2007 (see Figure 1.1) [1].

Consequently, more CO_2 has been released to the atmosphere causing global warming and other severe effects. The Energy Information Administration (EIA) estimated that, in 2005, net CO_2 emissions reached the threshold of 28 Gt and the same EIA expects that CO_2 emission could exceed 42 Gt by 2030 (see Figure 1.2) [1].

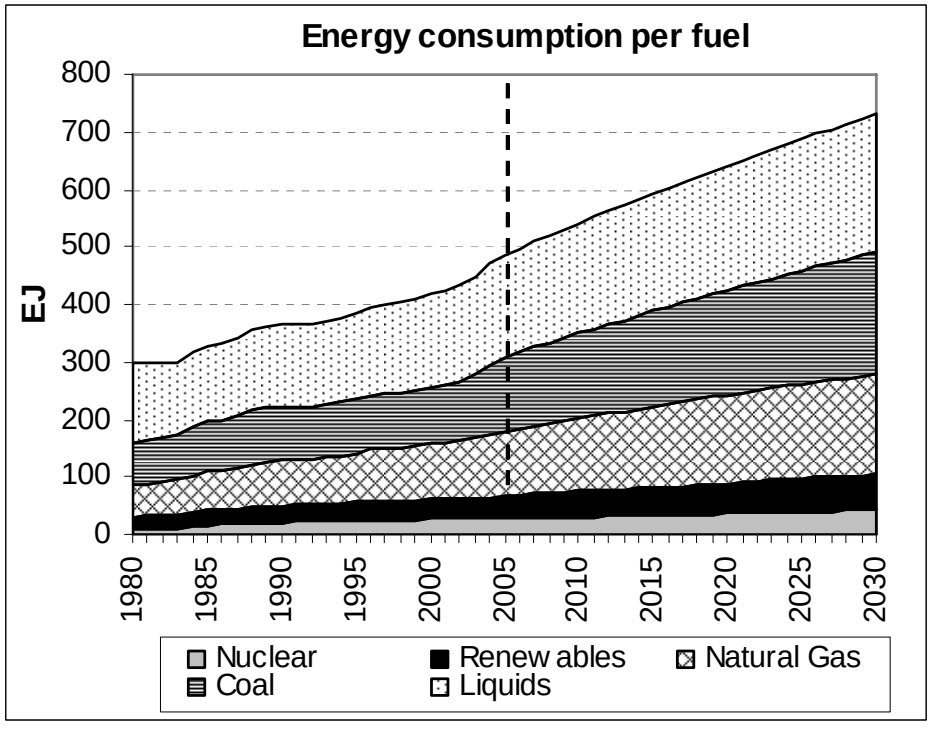


Figure 1.1. Energy consumption of different fuels. Values for period after 2005 are based on predictions. Adapted from data of the EIA world energy projections 2008 [1].

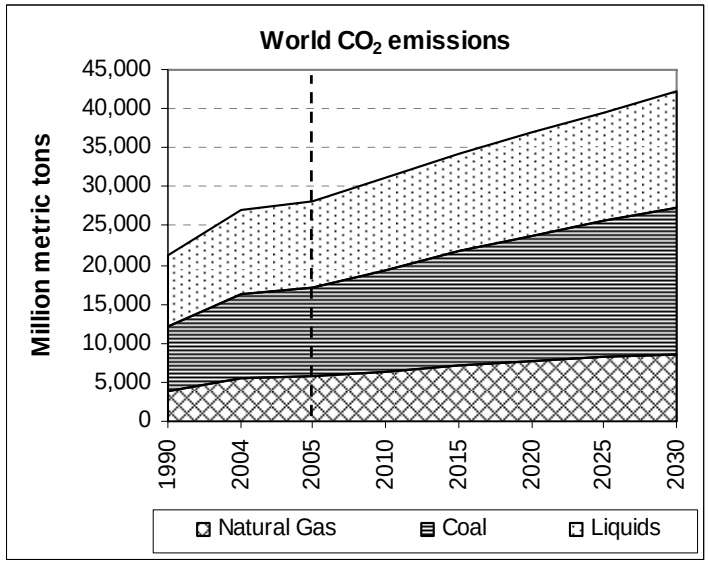


Figure 1.2. World CO_2 emissions. Values for period after 2005 are based on predictions. Adapted from data of the EIA world energy outlook 2008 [1].

As mentioned, another main disadvantage of fossil fuels, particularly oil and gas, is that their exploitation is controlled by few producer countries. Moreover, prices of fossil fuels are difficult to predict. Some factors, including reservoirs depletion, spot market speculation, and strategy of producer nations, play an important role when fixing the price of fossil fuels, especially for the case of crude oil. For the past years, however, the tendency is an irregular increase of crude oil prices (Figure 1.3). Natural gas and coal reserves are more distributed geographically (Figure 1.5), and the prices are better regulated at national level (Figure 1.4).

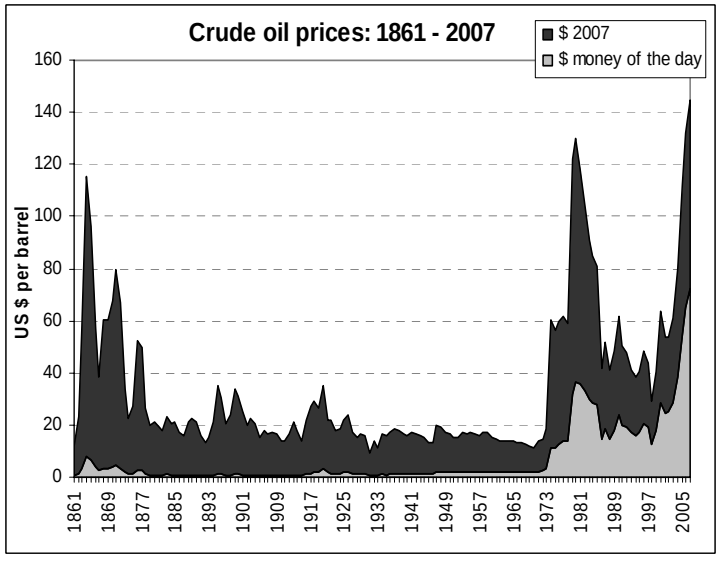


Figure 1.3. Crude oil prices for the period 1861-2007. Adapted from British Petroleum (BP) historical data [2].

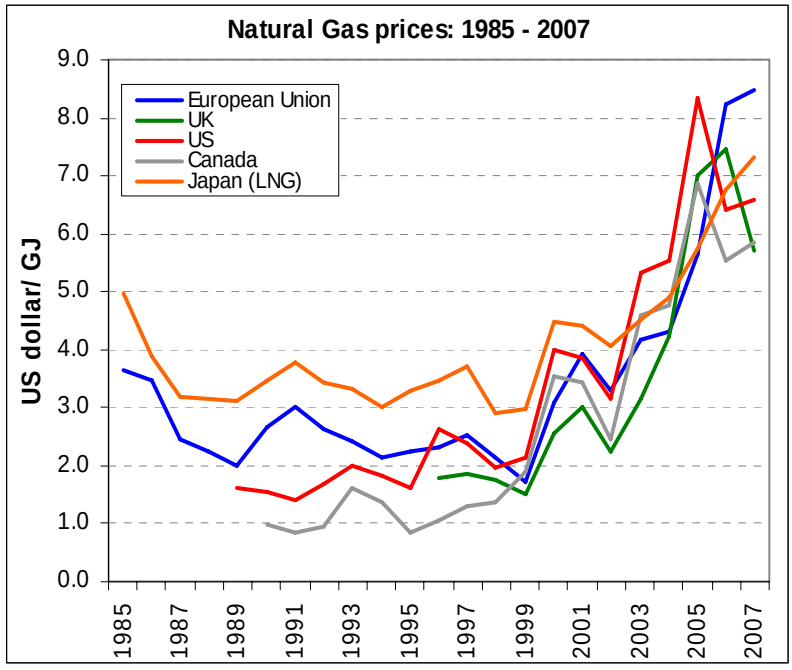


Figure 1.4. Natural gas process for the period 1980-2007. Adapted from British Petroleum (BP) historical data [2].

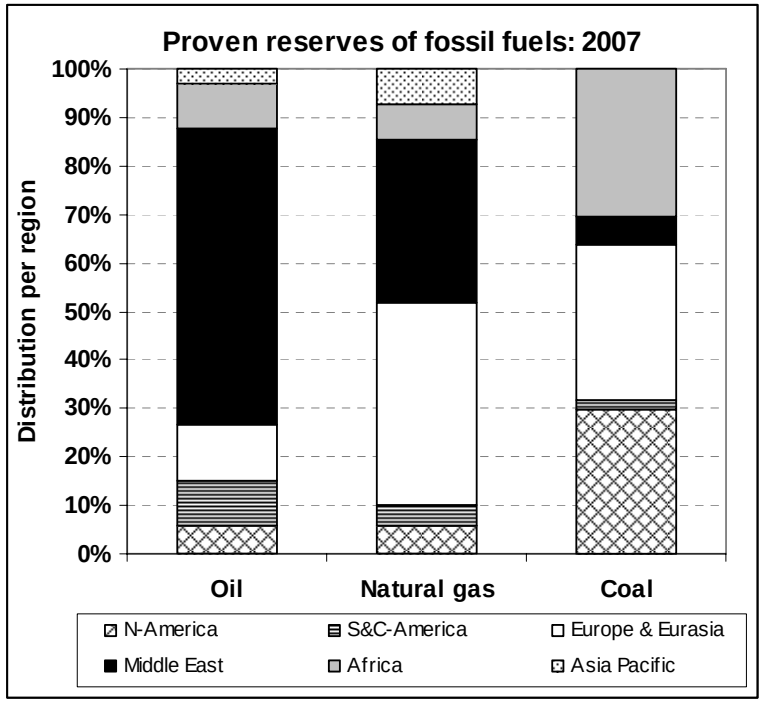


Figure 1.5. Fossil fuels reserves distribution per region. Adapted from British Petroleum (BP) historical data [2].

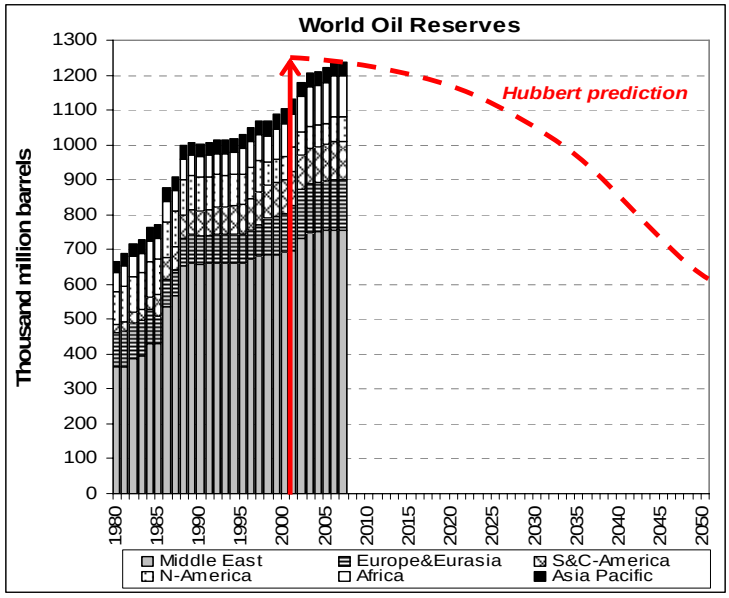


Figure 1.6. World Oil Reserves for the period 1980-2007. Adapted from British Petroleum (BP) historical data [2].

Some experts estimate that oil, natural gas and coal reserves will last for about 40-45, 100-200 and 400 years, respectively, at present consumption rate, although these numbers are continuously questioned by other scientists. Most of the theories dealing with the estimation of oil reserves have set the oil peak in the timeframe of 1995-2016 [3], including the earliest theory of the geophysicist Dr.M.K.Hubbert. He created his first prediction in 1956 in order to forecast the United States' oil peak production between 1965 and 1970. In 1974 he readjusted his own model and estimated that the production peak would arrive around 1995-2000. This Hubbert peak theory and its variants have been shown to be descriptive with reasonable accuracy of the peak and decline of oil production and reservoirs. According to this theory, oil production rate would follow a roughly symmetrical bell-shaped curve centered in the oil peak around 1995-2000 (see Figure 1.6). Later models based on current data and more complex functions are being developed, but the Hubbert curve profile remains unchanged, although the peak timeframe and the slope of the decline differs from model to model. For instance, the latest model of ASPO (Association for the Study of Peak Oil and Gas) places the oil peak in 2005. If heavy oil, deepwater, polar and natural gas liquids are considered then ASPO projects the oil peak for around 2010-2011.

1.2. Biomass and Wastes as Key Renewable Alternatives

For a more sustainable development, current energy consumption should be shifted to introduce more renewable sources such as biomass, wind, solar, hydropower or geothermal energy, which are also more evenly distributed in the world. However, renewable sources alone could not cover the total energy demand of the growing world's population, where the consumption per capita is increasing as well. It is also necessary to improve energy

conversion technologies for either fossil fuels or renewable sources. For instance, global efficiencies of electricity production average 34% for coal, 40% for natural gas and 37% for oil (International Energy Agency (IEA)). Using advanced integrated gasification combined cycles (IGCC), overall efficiency can reach values of 40-45%, i.e., 49-55% of the Carnot efficiency limit. This could be the case of using biomass as feedstock in an IGCC system, although existing biomass-based plants are still far from those targets (e.g., 32% of electrical efficiency in the Swedish Värnamo demonstration plant [4]). Other emerging renewable sources such as solar and wind energy achieve lower electrical efficiencies with present technologies. However, an opposite conclusion is drawn when the conversion efficiency of sunlight into chemical energy in biomass via photosynthesis is taken into account (i.e., 0.5-1% [5]). Commercial photovoltaic cells convert sunlight into electricity with an efficiency of 10-20%, and efficiencies up to 25% have been recorded in laboratories for crystalline silicone membranes. According to the Beltz's law, the theoretical maximum power efficiency of any wind turbine design is 59%, although the most advanced wind turbines do not exceed 35-45% of efficiency. Including inefficiencies of other components in a wind turbine system (e.g., generator, bearings or power transmission), only 10-30% of the wind power is actually converted into usable electricity. On the other hand, hydroelectric power attains the highest efficiency (i.e., 90%) and can be far less expensive than electricity generated from fossil fuels or nuclear energy. However, environmental concerns about the effects of reservoirs limit the development of economic hydropower sources.

Currently, biomass is the main renewable energy source in terms of energy production and consumption. Considering the 27 members of the European Union, biomass represented 68% of the renewable energy consumption in 2006, whereas in the Netherlands the share was even higher, i.e., about 94% (see Figure 1.7). The biomass contribution to renewable energy consumption in the United States was 48%, followed by hydropower at 42%. Wind and solar energy are also gaining interest but their implementation is still far below biomass and wastes conversion.

Biomass is a clean and renewable feedstock that could contribute to overcome the major problems associated to the use of fossil fuels. For instance, biomass itself is a carbon-neutral fuel because emissions from thermal treatments (e.g. combustion) can be completely offset by carbon captured in growing biomass. It can also improve long-term energy security and enhance socio-economic development of rural regions. Nowadays, biomass has a well-known potential for producing modern energy carriers, such as electricity, heat (steam) and transport biofuels. In fact, even though electricity and heat can also be produced from other renewable alternatives (such as solar or wind energy), biomass is the only available renewable option to produce transport biofuels. This is of a great importance since the transport sector represents a significant share of the world's energy consumption, and it is almost exclusively fuelled by fossil oils. In 2005, transport sector accounted for 27% of the CO_2 emissions [6]. In order to overcome this situation, governments are adapting energy policies to include a specific compulsory share of renewable sources, notably biomass and wastes, in the energy balance. For instance, the recent European Directive 2003/30/EC establishes that biofuels shall replace 5.75% of fossil fuels in the road transport sector in 2010, and about 10% in the year 2020 [7].

However, biomass has also some drawbacks mainly due to its low energy density. Therefore, biomass is labor-intensive, logistics costs are considerably high, elaborate pre-treatments steps (e.g., drying, size reduction, densification, etc) are frequently required, and the existing technology is not very efficient yet.

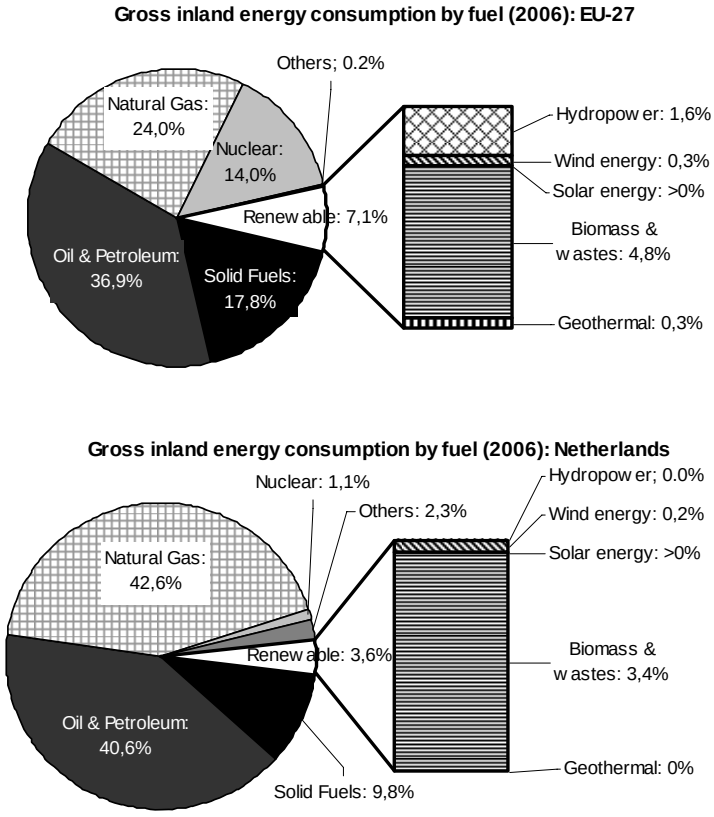


Figure 1.7. Gross energy consumption by fuel in the 27 members of the European Union compared to the Netherlands [Eurostat].

Local biomass availability can also be rather limited and stochastically distributed. This could become a major problem in industrialized countries where biomass could compete with other land uses, notably agriculture. Recently, biowastes are being regarded as a complementary alternative to energy crops to avoid food competition. Moreover, in some cases, wastes are not properly processed and existing treatments, such as incineration and landfilling, are even harmful for the environment. Biowastes costs are generally lower or even negative [8].

Several biowastes streams (such as verge grass, wood and agricultural residues, manure, sludge or even municipal wastes) can be used for biofuels production as well as heat and electricity. Biowastes can also be used in many different biochemical and thermochemical conversion technologies, yielding a wide range of biowastes-to-biofuels routes. Depending on the origin of the biomass source, biofuels are classified in two major groups: the so-called first and second generation biofuels (see Figure 1.8). First generation biofuels are characterized for using sugars or vegetable oils from dedicated food crops and converting them by biochemical methods. This is the case of bioethanol produced by fermentation and methyl esters (biodiesel) produced by chemical transesterification of vegetable oils. First generation technologies are well established and, in 2006, the global production of bioethanol and biodiesel achieved 39.5 and 5.4 million tones, respectively. However, when taking into

account emissions from transport and conversion treatments, life-cycle analyses reveal that first-generation biofuels frequently exceed the emissions threshold of fossil fuels.

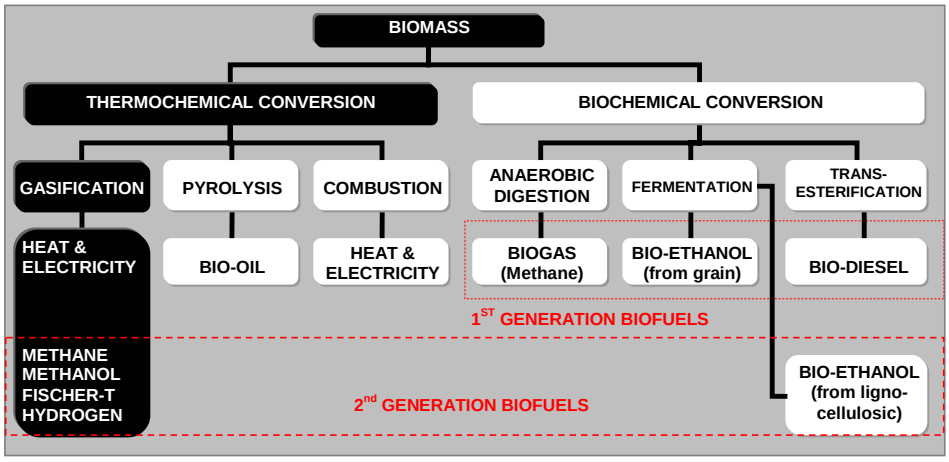


Figure 1.8. General overview of main 1st and 2nd generation biofuels and the corresponding conversion routes.

In order to overcome problems related to land competition between food and biofuels production as well as mitigate environmental impacts, different technologies are now being developed. This is the case of the so-called second generation biofuels that use non-edible feedstock such as lignocellulosic materials or biowastes from different sources (e.g., forest, agriculture, industry, municipalities). Hence, whole crops are consumed for biofuels production, which improves land area productivity and reduces GHG's emissions [9]. Moreover, plant production scales are projected to be higher.

Cellulosic bioethanol is obtained in a similar way as bioethanol produced from sugars or starch, but hydrolysis and saccharification steps are needed to convert lignocellulosic materials into a more convenient feedstock for alcoholic fermentation. Hence, the overall process is more complex and energy intensive. Plant capacities are expected to be in the range of 5–110 MW_{fuel} with an overall efficiency of about 45-50% [9].

Second generation biofuels like SNG, Fischer-Tropsch fuels, methanol and hydrogen can be produced principally via thermochemical methods. There are already some demonstration plants in the world, and there are also many plans for the commercialization of these fuels to larger scales. This is the case of CHOREN Industries GmbH that have already started building a Fischer-Tropsch plant in Germany with a capacity of 640 MW_{th} [10]. Among all existing thermochemical conversion technologies, gasification is reported to reach higher energy efficiencies, i.e., around 60-80% as cold gas efficiencies for wood gasification. Gasification is a thermal process that converts organic feedstock into a mixture of gases (syngas) using a limited amount of an oxidizing medium. The resulting syngas mainly consists of CO and H_2, but other gases can also be present (e.g., CH_4, CO_2, C_2H_4, or C_2H_6). However, the main drawback of gasification technologies is the formation of tars which remains as one of the most difficult technical barriers for gasification commercialization. In general, tars are a complex mixture of condensable hydrocarbons, and their amount and composition depend on the operational conditions and the gasifier design. Several

technologies exist for tars removal, including catalytic cracking, thermal cracking, plasma reactors or physical absorption. After cooling, cleaning stages and tar removal, syngas is further converted to biofuels by means of water-gas-shift reactors (WGS) and specific catalytic reactors. For methanol, Fischer-Tropsch fuels and hydrogen, the corresponding overall thermal energy efficiencies (Ψ_{HHV}) found in the literature are in the range of 33-59 % [9, 11-19]. For the case of SNG, higher efficiencies are obtained, i.e., 58-70% [9, 12, 15, 20-22]. Muller-Larger et al. compared the environmental impact of first vs. second generation biofuels in a Wheel-to-Well (WTW) analysis based on same kilometric distances (i.e., Kg of CO_2eq/km) [9]. Results revealed that SNG, Fischer-Tropsch, cellulosic bioethanol or biogas has a better potential for GHG's mitigation. However, WTW costs are slightly higher for most of the 2nd generation than for 1st generation biofuels.

1.3. Challenges for Biomass Energy Implementation

A wide range of biomass and wastes can be converted to biofuels via thermochemical, biological and even physical processes. Moreover, a broad range of biofuels can also be obtained with different composition, properties and functionality. Hence, there are several challenges to the development of biofuels that might compete with fossil fuels in a near future. Firstly, existing technologies must be adapted and improved to process biowastes in a more efficient way. Secondly, the most sustainable biowastes-to-biofuels routes have to be selected. Thirdly, final biofuels implementation must also be efficient and sustainable.

Many definitions about sustainability exist, but in a general sense, sustainability is defined as "*the capacity to maintain a certain process or state indefinitely*". Applied to the human community, sustainability has been expressed as "*meeting the needs of the present without compromising the ability of future generations to meet their own needs*" (U.S. Environmental Protection Agency). In our case, we consider that a sustainable process should efficiently use matter and energy, guarantee energy security, are respectful with the environment and the society as well as be economically feasible. Therefore, the sustainability of a process should be evaluated as a combination of 3 main parameters, i.e., process efficiency, economic and socio-environmental impact. In fact, there is a strong relationship among these 3 factors. For the same services or end-products, an efficient process will use less resources and cause less pollution. It will also be translated into a lower investment and operational cost. Sustainability framework is schematically represented in Figure 1.9.

Consequently, an inherent challenge is to develop a reliable model to evaluate the sustainability of any process. A proper model could determine whether biofuels are more beneficial than fossil fuels or other forms of renewable energy. However, sustainability methods are not standardized and many of them lack the aforementioned key factors, i.e., efficiency, economic and environmental impacts. This is the case of the so-called unidimensional accounting methods that measure the impact of each factor separately. More recently, multidimensional methods are considered to be more accurate as they intend to integrate the effect of each factor. For instance, increasing the efficiency of the process has also some benefits on the economic and environmental impact of the conversion route. However, excessive efficiency targets can be translated into extreme high costs, and thus, making the process impractical. Examples of unidimensional and multidimensional accounting methods are shown in section 7.

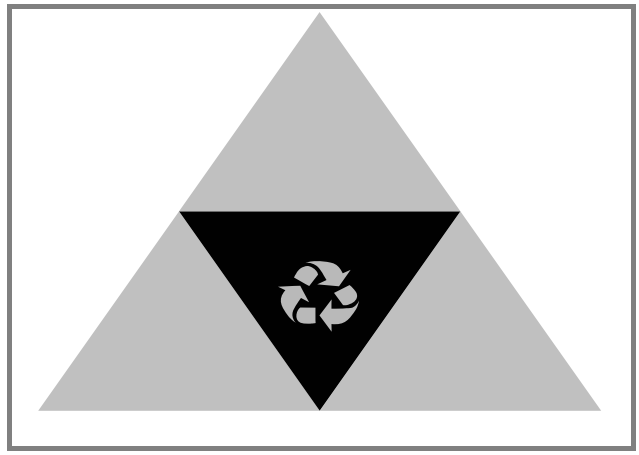


Figure 1.9. Representation of the sustainability concept.

1.4. Aim of the Chapter

In this chapter we present gasification as the core operation unit to effectively and efficiently produce second generation biofuels from different biowastes sources. Motivations for this choice are presented in the section 3. The selected biofuels are: Synthetic Natural Gas (SNG), methanol, Fischer-Tropsch fuels, hydrogen and heat-electricity. Our case study is the Dutch province of Friesland, and only biowastes generated in this region are considered. Biowastes are classified in five different streams according to their composition, i.e., wood and forest wastes, grass and organic wastes, agricultural wastes, manure and sludge, and municipal wastes (MSW).

In this chapter, the first factor "efficiency" is measured as "exergetic efficiency". In fact, for a sustainable development, we should consider both the quantity and quality of the energy used within a process. Traditional energy accounting methods based on the 1st Law of Thermodynamics have been questioned as they only take into account the principle of energy conservation. Energy efficiency indicators based on the 2nd Law of Thermodynamics are more accurate as they also comprise the quality (exergy) of the energy involved in any process. Exergy is defined as the maximum amount of work that can be produced by a stream or a system when it is brought into equilibrium with a reference environment. Hence, exergy is conserved in ideal processes but it is consumed in real processes. This exergy consumption is directly proportional to the entropy generated due to irreversibilities. Many researchers have suggested that the thermodynamic efficiency could be better evaluated when using an exergy analysis [23, 24].

Exergy results will be used later for the economic and socio-environmental impact analysis. However, economic and socio-environmental analyses are not presented in this chapter, but some values found in literature will be discussed in section 7. In our future research, these 3 factors will be then combined by using multidimensional methods such as Extended Exergy Accounting (EEA), Thermo-Economics, and an own sustainability method will be finally formulated to properly assess the sustainability of any process.

1.5. Outline of the Chapter

This chapter is structured in several sections for a better readability. Section 2 is devoted to introduce the composition and peculiarities of the biowastes streams used in our evaluation. Subsequent section 3 is dedicated to explain the main features of standard biomass gasifiers. In this section, different gasifier designs and operation modes are discussed. Gasification efficiency is calculated by means of an exergy analysis, and the effect of several operational parameters (such as temperature, pressure, heating and gasifying agents) is evaluated and compared with data found in literature. Section 4 contains detailed information about the design and simulation of 5 biofuels in Aspen Plus whereas section 5 presents the main applications of these biofuels in the market. Efficiency and sustainability of the 5 biowastes-to-biofuels conversion routes are evaluated in section 6. Subsequent section 7 shows the architecture of the Decision Support System (DSS) that is designed to eventually identify the most sustainable biowastes-to-biofuels routes for a particular region, e.g., Friesland. The DDS will finally result in a Master Plan that could be used for strategic decisions of the involved companies and for regional policy making. Finally, main conclusions are gathered in the last section 8.

2. BIOMASS AS A SUSTAINABLE ENERGY SOURCE

Biomass commonly refers to any living or recently dead biological material but it also includes other biodegradable biowastes such as manure and sewage sludge. The term excludes organic materials which have been transformed by geological processes into substances such as coal or petroleum. Hence, biomass and biowastes comprises a wide spectrum of heterogeneous feedstock whose composition may vary depending on its origin, local conditions, season and other factors. Moreover, their availability, cost and even social acceptance is subjected to regional circumstances.

2.1. Global Availability and Potential of Biomass

About 115-120 billion tons of biomass is formed each year by means of photosynthesis in continental ecosystems [25, 26]. This would represent around fivefold of the total energy consumption in the world (i.e., 400 EJ in 1998 [1]) in the unfeasible scenario that readily available biomass sources were converted to energy. Biomass use covers less than 14% of the global energy demand [27, 28] but some governmental policies have set higher values for the near future, including all 27 European Union countries, 29 U.S. states and 9 Canadian provinces. Most of these targets refer to shares of electricity production, primary and/or final energy use, and they aim for the 2010–2012 timeframe, although an increasing number of targets have also been set for 2020. In particular, the European Commission establishes that 20% of the primary energy supply in 2020 should be delivered by renewable energy sources, notably biomass. In the Netherlands, the value is fixed to 10% (288 PJ) and about 42% of this target is to be achieved by biomass and wastes (75 and 45 PJ, respectively) [20]. In addition, there are also specific targets for biofuels share in the transport sector, including the European

Directive 2003/30/EC that establishes 10% of biofuels share by 2020 [7]. Different global scenarios studies have questioned the viability of these targets and even a higher contribution of biomass to global energy consumption. In general, biomass contribution has been estimated in the broad range of 33 to 1135 EJ/year by 2050 [29, 30], although more optimistic studies has fixed this number to 300-657 EJ/year, i.e., 40-60% of the energy demand in 2050 [31].

However, biomass availability is rather limited and stochastically distributed. This is a major problem in most industrialized countries where land is scarce and biofuels may compete with other land uses, notably agriculture for food production. The use of biowastes instead of biomass derived from energy crops could overcome this situation. Moreover, biowastes costs are often much lower or even negative [8]. Mengjie et al [26] estimated that about 111 EJ/year could be produced from forest and agricultural residues (see Table 2.1), which would contribute to about 20% of the global energy demand in 2010 (considering 512 EJ energy demand by 2010 [1]). Other authors estimates that forest, agricultural residues and other wastes can supply 30 to 90 EJ/year in 2020-2050 at low costs [32].

Table 2.1. Annual Biomass Energy Yield from Residue in Different Areas in the World in 1987 unit: EJ (10^{18} J) [26]

Area	Maize Straw	Wheat Straw	Rice Straw	Bagasse	Manure	Forest Residue	Firewood Forest	Total
Industrialized countries and areas								
USA and Canada	2.95	1.93	0.13	0.19	3.08	7.66	0.92	16.86
Europe	0.61	2.39	0.04	0	4.22	4.12	0.41	11.79
Japan	0	0.02	0.24	0.01	0.3	0.41	0	0.98
Australia	0	0.29	0.02	0.19	1.36	0.35	0.02	2.23
and New Zealand	0.23	1.97	0.04	0	3.58	3.92	0.6	10.34
Total	3.8	6.6	0.5	0.4	12.5	16.5	1.9	42.2
Developing countries and areas								
Latin America	0.71	0.38	0.29	3.58	7.21	1.47	2.12	15.76
Africa	0.48	0.25	0.2	0.54	5.38	0.75	3.31	10.91
China	1.23	1.75	3.43	0.48	4.81	1.27	1.34	14.31
Other Asian countries	0.51	1.88	5.29	2.7	10.91	2.31	4.62	28.22
The Pacific	0	0	0	0.03	0.02	0.05	0.04	0.14
Total	2.9	4.3	9.2	7.3	28.3	5.8	11.4	69.2
Total in world	6.7	10.9	9.7	7.7	40.8	22.3	13.3	111.4

These biomass streams mainly differ in their chemical composition, heating value, ash and moisture content. Accessible databases such as Phyllis [33] and EERE (U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy [34]) have listed the composition and properties of many biomass feedstocks. Comparison of the biowastes

sources from our case study (see Table 2.3) reveals that higher heating values moderately vary (standard deviation of 13%), but a larger variation is observed for moisture and ash content (standard deviation of 33% and 55% respectively). Similar trends are observed when comparing a larger sources of materials [35].

Hence, in general, two sorts of biomass sources can be distinguished: dry and wet streams. Dry streams may comprise wood, straw and wastes from food industries whereas wet streams may consist of grass, organic fraction of municipal wastes, garden wastes, manure or even sewage sludge.

Normally, dry streams are preferred for thermal conversion technologies such as combustion, pyrolysis or gasification, and the analysis conducted in section 3 confirms this expectation. In fact, for wet streams, overall energy efficiency is negatively affected by the energy required to evaporate the moisture content of the fresh inlet biowaste.

Moreover, less biofuel is obtained from wet streams for the same amount of feedstock than dry streams. A report from the European Commission has also stated that dry streams such as woody and SRF (short rotation forest) wastes together with RDF (refused derived fuel) have a higher market potential and are more reliable for gasification applications [36]. Conversely, fibrous sources such as straw and grass are projected to be the worst option (see Figure 2.1).

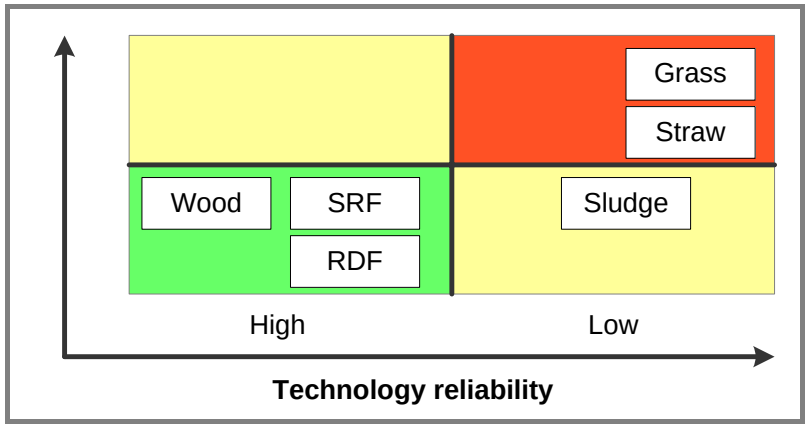


Figure 2.1. Status of feedstock technology reliability and market potential.

2.2. Biomass Supply-Costs

Biomass supply costs are directly affected by local conditions, especially availability, land uses, transport distances, policies and subsidies. Cost-supply curves of biomass feedstocks have been studied by many authors at regional [37], national [38] and global scale [29, 39], especially for energy crops in either dedicated or abandoned lands.

However, less information can be found for the other biomass and wastes streams as the market is still somewhat immature. Table 2.2 summarizes biomass and wastes supply-costs that exist in literature for the Netherlands. These values are taken for our case study.

Table 2.2. Average supply-cost/prices for biomass and wastes from literature

Feedstock	Region	Supply-cost/price	Year	Source
Energy crops	Netherlands (EU)	6.1 – 7.8 €/GJ_{HHV}	2010	Rabou et al. [40]
		3.5 – 4.8 \$/GJ_{HHV}	1997	Faaij et al. [41]
	Europe	2.5 – 16.4 \$/GJ_{HHV}	2000	Hoogwijk et al. [39]
	USA	2.1 – 7.4 \$/GJ_{HHV}	2000	Hoogwijk et al. [39]
	Latin America	1.0 – 5.0 \$/GJ_{HHV}	2000	Hoogwijk et al. [39]
	Asia	0.5 – 1.3 \$/GJ_{HHV}	2000	Hoogwijk et al. [39]
Wood wastes	Netherlands (EU)	2.5 – 7.0 €/GJ_{HHV}	2006	Junginger et al. [42]
		0.0 – 5.2 €/GJ_{HHV}	2010	Rabou et al. [40]
		0.0 – 3.5 \$/GJ_{HHV}	1997	Faaij et al. [41]
Wood pellets	Netherlands (EU)	8.5 – 15.7 €/GJ_{HHV}	2006	Junginger et al. [42]
Agricultural wastes	Netherlands (EU)	Straw: 3.0 €/GJ_{HHV}	2010	Rabou et al. [40]
		Straw: 1.9-7.6 \$/GJ_{HHV}	1997	Faaij et al. [41]
		3.6 €/GJ_{HHV}	2006	Junginger et al. [42]
		00. – 1.5 \$/GJ_{HHV}	1997	Faaij et al. [41]
Manure	Netherlands (EU)	negative €/GJ_{HHV}	2006	Junginger et al. [42]
	Netherlands (EU)	~ 0 €/GJ_{HHV}	2010	Rabou et al. [40]
Sludge	Netherlands (EU)	negative €/GJ_{HHV}	2010	Rabou et al. [40]
		negative \$/GJ_{HHV}	1997	Faaij et al. [41]
Verge grass	Netherlands (EU)	negative 0 €/GJ_{HHV}	2010	Rabou et al. [40]
		0.0 – 0.8 \$/GJ_{HHV}	1997	Faaij et al. [41]
Organic household waste	Netherlands (EU)	negative 0 €/GJ_{HHV}	2010	Rabou et al. [40]
		negative 0 \$/GJ_{HHV}	1997	Faaij et al. [41]
Vegetable oil	Netherlands (EU)	18.6 €/GJ_{HHV}	2010	Rabou et al. [40]
Oil seed residues	Netherlands (EU)	10.0 €/GJ_{HHV}	2010	Rabou et al. [40]
Fatty acids and animal fats	Netherlands (EU)	2.0 – 10.0 €/GJ_{HHV}	2010	Rabou et al. [40]
Dry food industry wastes	Netherlands (EU)	3.2 €/GJ_{HHV}	2010	Rabou et al. [40]
		~ 0 €/GJ_{HHV}	1997	Faaij et al. [41]
Municipal wastes	Netherlands (EU)	~ 0 €/GJ_{HHV}	2010	Rabou et al. [40]

2.3. Case study: Biomass from Friesland Province

Due to low density of biomass and wastes, local use of biomass should be preferred. The northern Dutch province of Friesland has been taken here as a case study to evaluate the potential conversion of biowastes-to-biofuels for a specific region. Friesland (Fryslân) is a province located in the north-east of the Netherlands, which consists of 31 municipalities and 3 islands in its northern coast (i.e., Vlieland, Ameland and Terschelling), although Texel and Schiermonnikoog islands are also included in our study. Traditionally, this area accounts for a large amount and range of biowastes that could be better processed to obtain energy and avoid unsustainable practices like landfilling or incineration. For our purpose, all biowastes streams from Friesland has been analyzed and gathered in 5 “virtual” streams (named “A” to “E”). This classification has been made according to their corresponding ultimate and proximate analysis (see Table 2.3). Compositions are obtained from Phyllis database [33] and weighted by each substream. However, for the exergetic analysis and mass conversion

comparison, the amount of all streams is fixed to 57,000 kg feedstock/hr. Real amounts will be taken into account in future studies aiming in the final Master Plan by 2010.

Table 2.3. Ultimate, proximate analysis and annual production of the Frisian biowastes streams. Composition values are given on a dry basis (db %). Biowastes amounts are given on wet basis, i.e., fresh feedstock

Nomenclature ➡	Stream A:	Stream B:	Stream C:	Stream D:	Stream E:
Biowaste stream ➡ Parameter (d.b.%) ⬇	Wood and forest w aste	Grass and organic wastes	Agricultural and f and b[(a)] wastes	Manure and sludge	Municipal solid wastes (MSW)
Ultimate and proximate analysis					
C (wt %)	49.04	39.60	42.30	29.91	40.42
H (wt %)	5.74	4.70	5.10	4.30	4.97
N (wt %)	1.61	1.60	1.50	2.96	0.91
Cl (wt %)	0.096	0.460	0.390	0.967	0.950
S (wt %)	0.084	0.200	0.250	0.623	0.350
O (wt %)	39.41	33.70	35.10	22.43	25.30
Ash (wt %)	4.02	19.74	15.36	38.80	27.10
Moisture (wt %)	13.80	33.50	26.10	43.40	30.70
HHV(kJ/kg)	19,789	16,073	18,086	13,019	16,527
Annual production (kton/year)					
Province	91	155	212	5359	114
Islands	15	3	1	27	5

(a) f&b: wastes from food and beverages industries.

Frisian biowastes prices are estimated from the values found in literature for the Netherlands (Table 2.2) and weighted by each substream (see Table 2.4). These values will be integrated into a later economic analysis of 5 different biowastes-to-biofuels routes in the corresponding TOC (total operation costs).

Table 2.4. Unit and annual supply-costs for the cases of the Friesland province and the Wadden Islands. Transport costs related to ship transfer from the Wadden Islands to the province are not incorporated here

Nomenclature ➡	Stream A:	Stream B:	Stream C:	Stream D:	Stream E:
Parameter (d.b.%) ⬇	Wood and forest waste	Grass and organic wastes	Agricultural and f and b[(a)] wastes	Manure and sludge	Municipal solid wastes (MSW)
Supply-costs (unit price in €/GJ_{HHV})					
Province	0.70 €/GJ_{HHV}	-1.27 €/GJ_{HHV}	1.01 €/GJ_{HHV}	~ 0 €/GJ_{HHV}	~ 0 €/GJ_{HHV}
Wadden Islands	0.70 €/GJ_{HHV}	-1.27 €/GJ_{HHV}	1.01 €/GJ_{HHV}	~ 0 €/GJ_{HHV}	~ 0 €/GJ_{HHV}
Annual supply-costs (€/year) associated to biowastes on-site delivery					
Province	1,333,259 €	-4,431,313 €	4,967,471 €	0 €	0 €
Wadden Islands	170,000 €	-122,001 €	59,493 €	0 €	0 €

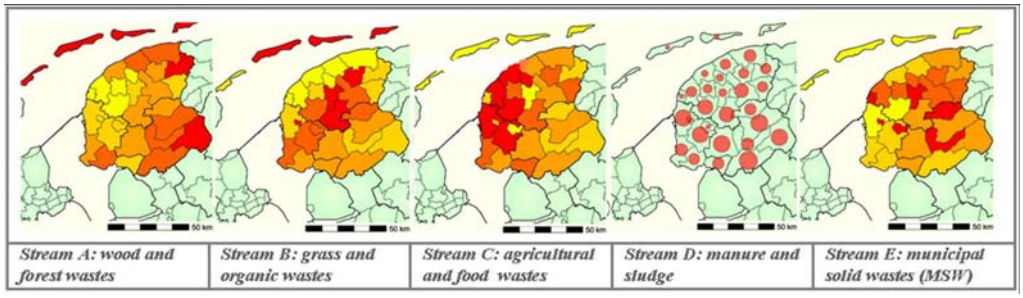


Figure 2.2. Biowastes density production within the Friesland province. Darker colors represent higher amount of biowastes. Data has been taken from Centraal Bureau voor de Statistiek (Statistics of the Netherlands) [43].

On the other hand, Frisian biowastes have been located within the province in order to calculate transport between the collection points and the processing plant has been taken into consideration. For this analysis, it is assumed that biowastes are generated continuously all throughout the year. Figure 2.2 show the density amount of each biowaste stream per municipality, where darker colors represent a high amount of biowastes production.

3. GASIFICATION TECHNOLOGY FOR BIOMASS CONVERSION

Gasification is an old process that was originally developed in the 1800s to produce town gas from coal for lighting and cooking, but subsequent natural gas exploitation soon replaced this "town gas". Petroleum shortage during World War II brought a resurgence of gasification technologies when wood, and later coal, were gasified to produce liquid fuels for the vehicles. After the war, most of the gasifiers were mothballed as inexpensive petroleum was widely available. However, the oil crisis in the 1970's and 1980's motivated new research and development on coal gasifiers. Nowadays, environmental concerns about global warming have shifted the focus from coal to biomass gasification. Gasification is a thermochemical process that converts carbonaceous materials by heating them at high temperatures and under a controlled amount of oxidizers. It is a partial oxidation process in a sense that the oxygen added is less than the stoichiometric amount required for complete combustion. The resulting gas mixture is called synthesis gas or syngas, which mainly contains CO and H_2. Syngas itself is a fuel as it can be directly burned in internal combustion engines or further processed to produce chemicals, liquid fuels, SNG or hydrogen.

Among all the existing thermochemical methods, gasification has gained more interest as it offers higher efficiencies compared to combustion whereas fast pyrolysis is still at a relatively early stage of development [44]. Compared to biochemical conversion technologies, gasification has also many advantages. For instance, unlike bioethanol and biodiesel that are mainly produced from clean energy crops or lignocellulosic materials, gasification can process a wider range of biowastes, including more heterogeneous and polluted streams like MSW. This has a clear relevance since MSW represent an important fraction of the wastes collected in municipalities and rural areas. Biofuels obtained via thermochemical methods, in particular gasification, also have better qualities for the transportation section than biochemical derived fuels (see Table 3.3). When comparing the

efficiencies of existing processes, syngas derived biofuels (e.g., methane, methanol, Fischer-Tropsch fuels and hydrogen) also achieve higher values (see Table 3.1).

Table 3.1. Comparison of biochemical and thermochemical biofuels in terms of production efficiency

Technology	Biofuel	Production efficiency	References
Biochemical	Bioethanol from grain	Ψ_{HHV}: 38%	[11]
	Lignocellulosic bioethanol	Ψ_{HHV}: 35%	[11]
Thermochemical (gasification)	Methane (SNG)	Ψ_{HHV}: 58-70%	[9, 12, 15, 20-22]
	Methanol	Ψ_{HHV}: 40-59%	[9, 11-14]
	Fischer-Tropsch	Ψ_{HHV}: 33-56%	[9, 15-19]
	Hydrogen	Ψ_{HHV}: 45%	[11, 13]

However, one of the main disadvantages of gasification is the formation of tars. In general, tars are defined as being a complex mixture of condensable hydrocarbons. When biomass is heated, the molecular bonds of the biomass break into the larger molecules formed the so-called “primary tars”. These primary tars can then react to secondary tars by more complex reactions at the same temperature and to tertiary tars at high temperature. Figure 3.1 shows a tar formation pathway proposed by Basu [45].

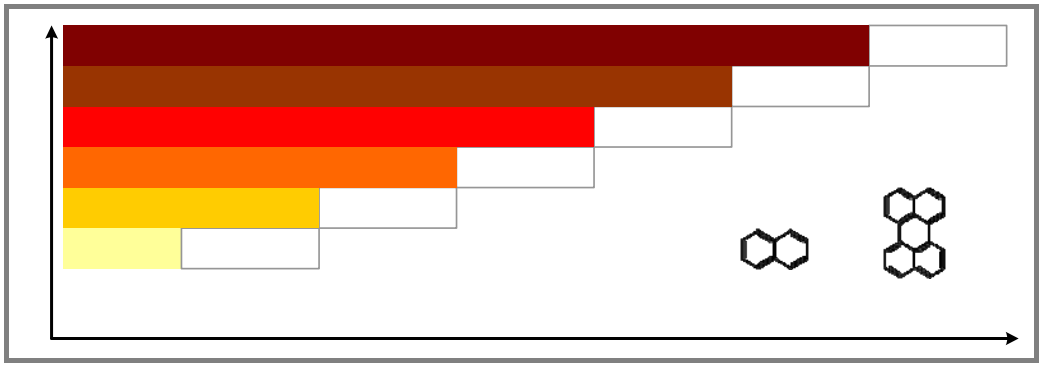


Figure 3.1. Tar formation within the temperature profile occurring in the gasifier. (PAH=Polyaromatic hydrocarbons).

Tar formation is a major problem in gasification systems and remains as one of the most difficult technical barriers. Table 3.2 presents the classification of tars based on the potential problems that can occur in other downstream units.

Tars can be removed from the product syngas by either chemical or physical methods. In chemical methods tar are decomposed to smaller molecules. Examples of chemical methods are catalytic cracking, thermal cracking, plasma reactors and catalytic bed materials. Among them, catalytic cracking has the advantage that the heating value of the tar is conserved as it is converted to other gases [45]. Calcined dolomite and nickel-based catalyst are commonly used for this purpose. Conversely, physical methods completely remove the tars from the

syngas but a new notably-polluted waste stream is then generated. Typical physical devices are cyclones, filters, electrostatics precipitators and scrubbers.

Table 3.2. Tar classification system based on the behavior of tar compounds in downstream units. Adapted from [46]

Type	Category	Chemical group	Examples	Behavior
Primary tars	Class 1	Oxygenated compounds	GC*-undetectable, but heavier than corosene	*Not identified compounds.*
Secondary tars	Class 2	Heterocyclic aromatics	pyridine, phenol, quinoline	Compounds with the highest water solubility.
	Class 3	Aromatic (1 ring)	xylene, styrene, toluene	Compounds that do not contribute to condensation or solubility problems.
Tertiary tars	Class 4	Light PAH (2-3 rings)	naphtalene, biphenyl, fluorene, phenanthrene, anthracene	Condensate at high concentrations and intermediate temperatures.
	Class 5	Heavy PAH (4-7 rings)	fluoranthene, pyrene, chrysene, benzopyrene, perylene	Condensate at low concentrations and high temperatures.

(*) GC: it refers to a particular method for tars detection.

Energy research Centre of the Netherlands (ECN) has also developed a new technology for tars removal, based on syngas scrubbing with oil. The principle is similar to a physical tar removal method but in this case, by using an special oil, tars can be recycled to the gasifier and destructed herein, which in turns avoids the problematic handling of waste streams [47].

3.1. Gasification Reactions

The complexity of the gasification process is illustrated by the number of reactions taking place, and the considerably number of components in the biomass.

In Table 3.3 the main reactions in the gasification process are listed. As observed, the most relevant equations for carbon conversion are (2), (6) and (10), which also yield most of the CO and H_2 (main syngas compounds) [48]. Gas-solid reactions of char oxidation are the slowest and, hence, they limit the overall rate of the gasification process. On the other hand, more H_2 can be produced in the WGS reaction at expenses of CO and H_2O (Eq. (5)). In order

to achieve a high thermodynamic efficiency, exothermic reactions should be coupled with the endothermic reactions (9) and (10).

Table 3.3. List of main gasification reactions

Reaction	Equation	ΔH_{298} (kJ/mol)	Eq. no
Decomposition	$Volatile\ matter \rightarrow CH_4 + C$	Mildly exothermic	*(1)*
Partial combustion	$C + 0.5O_2 \leftrightarrow CO$	-111	(2)
Combustion	$CO + 0.5O_2 \leftrightarrow CO_2$	-254	(3)
Combustion	$H_2 + 0.5O_2 \leftrightarrow H_2O$	-242	(4)
Water-gas-shift (WGS)	$CO + H_2O \leftrightarrow CO_2 + H_2$	-41	(5)
Methanation	$C + 2H_2 \leftrightarrow CH_4$	-75	(6)
Methanation (reverse of steam reforming)	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-165	(7)
Methanation	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-206	(8) = (5) + (7)
Water-gas	$C + H_2O \leftrightarrow CO + H_2$	+131	(9)
Boudouard	$C + CO_2 \leftrightarrow 2CO$	+172	(10)

3.2. Types of Gasifiers

The reactors used for gasification are very similar to those found in combustion processes. The main reactors types can be classified into three main groups depending upon the flow conditions:

- Entrained flow gasifiers
- Fluidized bed gasifiers, subdivided into bubbling (BFB) and circulating (CFB) beds.
- Fixed bed gasifiers, subdivided into counter-current (updraft), co-current (downdraft) and cross-current moving beds.

The reactors can be operated at atmospheric pressure or at higher pressures, but the latter is only available to BFB or CFB reactors. Pressurized equipments entail higher costs and higher safety risk of operation but these disadvantages can be compensated downstream by the smaller equipment size and higher reactivity. In 2003, Bridgwater *et al*. [44] estimated and compared the technology strength and market attractiveness for the main different types of gasifiers. His findings are presented in the Figure 3.2.

According to Bridgwater [44], CFB are the most reliable system for large scale plants whereas fixed bed gasifiers are more convenient for small applications due to their inability to keep uniform radial temperatures profiles and avoid local slagging problems. However, it should be noticed that Figure 3.2 may not be a proper representation for a near future as

entrained bed gasifiers can be improved, and hence, they can gain positions in market attractiveness and technology strength.

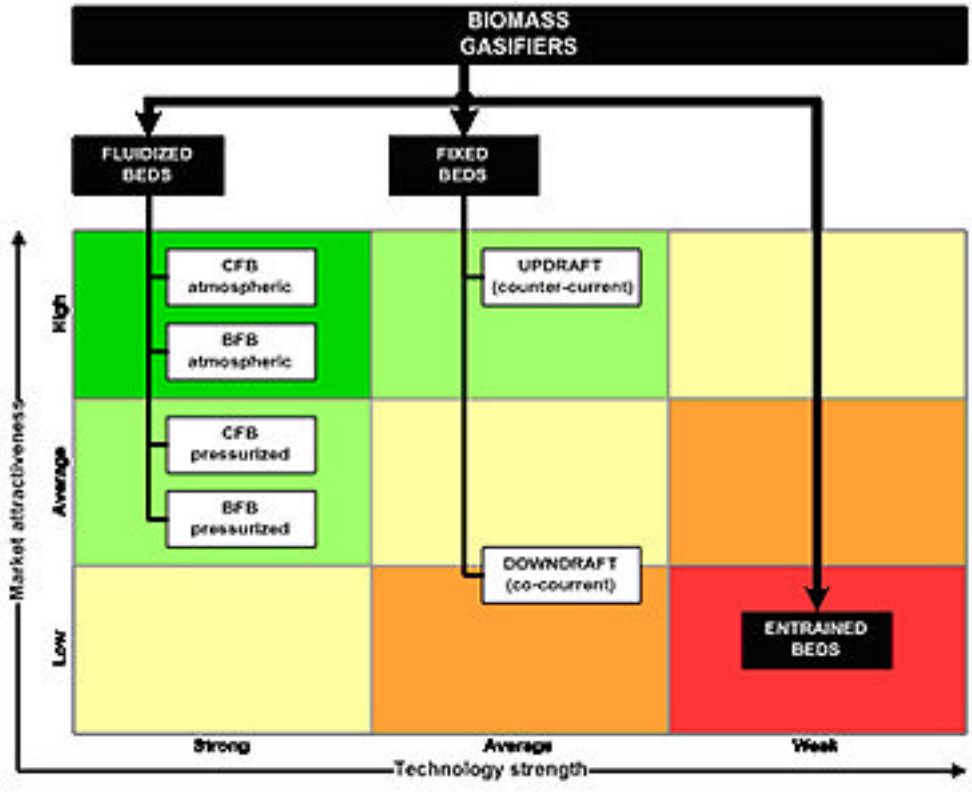


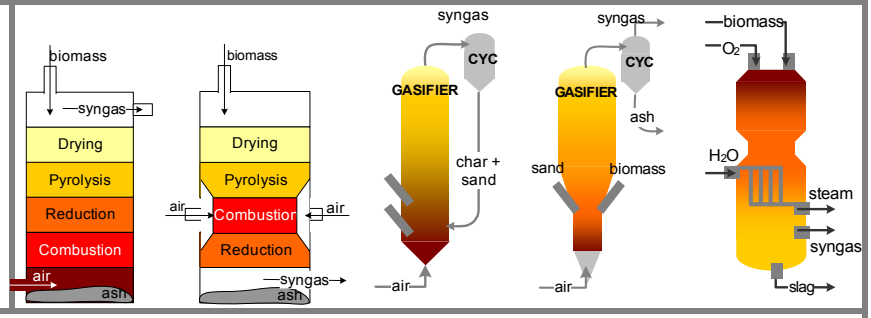
Figure 3.2. Comparison of market attractiveness and technology strength of different gasifiers [44].

CFB gasifiers are an extension of BFB concept, with the difference that with cyclones or other separators are employed to capture and recycle solids in order to extend the solids residence time. CFB have been successfully demonstrated up to 100 MW, and they are also expected to be stable and reliable at higher power ratings. Atmospheric BFB gasifiers are proven reliable up to 25 MW, but larger reactor size makes up-scaling difficult. Despite this fact, currently, downdraft (co-current) gasifiers account for about 75% of the manufactured gasifiers worldwide, 20% are fluidized beds (CFB and BFB), 2.5% are updraft gasifiers (counter-current) and the remaining 2.5% goes for other types [36]. The feedstock requirements, mode of operation, and output products obtained in each gasifier type are compared in Table 3.4.

3.3. Mode of Operation

The syngas compositions as well as the efficiency of the gasifier are directly affected by the gasifying medium (oxidizer), the operating conditions (e.g. temperature, pressure) and the mode of heating the gasifier (directly or indirectly). The effect of each parameter is presented in sections 3.4.1 to 3.4.5.

Table 3.4. Comparison of different types of gasifiers. Data adapted from [44] and [49-51]

Gasifiers types ➡	Fixed beds		Fluidized beds		Entrained flow
	Updraft	Downdraft	CFB	BFB	
Parameters ⬇					
Feedstock characteristics					
Particle size	5 – 100 mm	20 – 100 mm	0 – 20 mm	0 – 20 mm	< 100 µm
Ash tolerance	Max. 6%	Max. 6%	Max. 25%	Max. 25%	Max. 25%
Moisture content	Max. 60%	Max. 35%	-	-	-
Operational conditions					
Oxygen demand	Low	Low	Moderate	Moderate	High
Steam demand	High	Low	Moderate	Moderate	High
Feed-blast flow	Counter-current	Co-current			
Temperature	800-1000°C (less uniform)	1000-1200°C (less uniform)	750-950°C (more uniform)	900-1000°C (more uniform)	1100-1500 °C
Operating pressure	Atmospheric	Atmospheric	Atmospheric or pressurized	Atmospheric or pressurized	Atmospheric or pressurized
Feeding pressure	7 – 70 kPa	35 – 1050 kPa	7 – 35 kPa	7 – 35 kPa	7 – 350 kPa
Gas velocity	Low	Low	Higher than BFB	High	High
θ time	Long (15-30 min)	Long (15-30 min)	Short (5-50s)	Short (5-50s)	Very short (1-10s)
Product characteristics					
Temperature gas	425-650°C	425-650°C	900-1050°C	900-1050°C	1250-1600°C
HHV (air-blown)	5 – 6 MJ/Nm^3	4.5 – 5 MJ/Nm^3	~ 5 MJ/Nm^3	~ 5 MJ/Nm^3	-
Tar content	Very high 0.015–0.500 g/Nm^3	Low 0.015–0.50 g/Nm^3	Moderate <5 g/Nm$_3$	Moderate <5 g/Nm$_3$	Almost free
Plant					
Turndown ratio	5-10	3-4	3	3	-
Scale-up gasifier	Limited	Limited	Possible	Possible	Possible
Thermal capacity	< 10 MW	1kW – 10 MW	1 -100 MW	1 – 25 MW	-

3.3.1. Gasifying Medium

There are mainly 3 gasifying media or blasts, i.e., air, steam and pure oxygen, although other agents like CO_2 or H_2 are also being studied. Hence, the blast always contains oxygen, either as free oxygen or bound as for steam or CO_2. Biomass oxygen-blown gasification lead to the production of a syngas with medium heating value (10-13 MJ/Nm^3) but it is affected by high economic and investment costs and, hence, it is not implemented in commercial applications yet. However, the use of oxygen is still under consideration as it offers other benefits compared to air. For instance, product gases are not diluted with nitrogen, downstream equipments are smaller and compression stages require less energy. Steam-blown gasification is being the subject of numerous recent studies as it also produces a syngas with an acceptable HHV value (10-16 MJ/Nm^3).

The choice of the gasifying medium is also motivated by the desired composition of the end-product. In effect, steam contains hydrogen atoms and this results in a higher production rate of methane than when using air or oxygen. Hence, steam is the preferred gasifying media when the desired end-product is the production of SNG. Conversely, air (or oxygen if justified) is preferred for the production of BTL fuels, such as methanol or Fischer-Tropsch fuels, as less methane is formed and more CO and H_2 is available for producing methanol or hydrocarbons (Eq.(30-34)). The amount of added air or steam also affects the energy contained in the produced syngas and, in turn, the efficiency. The gasifying agent effect was studied by Prins *et al*. [48] who identified that the exergetic efficiency of air gasification is sensitive to the equivalence ration of air (ER) whereas the exergetic efficiency of steam gasification is not significantly influenced by the steam:biomass ratio, when steam is produced within the process. Moreover, the optimum exergetic efficiency of steam gasification is higher than the optimum efficiency of air gasification. For this analysis, exergetic efficiency is defined as the ratio of the desired output over the required input. For air gasification, in particular, optimum results are obtained when working at the carbon boundary, i.e., the point when all the carbon is converted [52]. Results from our simulations are in agreement with all these observations (see section 3.4).

3.3.2. Heat Transfer

The conversion of biomass to a low- or medium-heating-value gaseous fuel in a gasifier generally involves several processes. The first process is the drying step where water evaporates using the heat released from later stages. The dried biomass then undergoes pyrolysis reactions, which releases the volatile components of the feedstock at temperatures below 600°C via a set of complex reactions. These volatile vapors contain hydrocarbon gases, hydrogen, carbon monoxide, carbon dioxide, tars, and water vapor. The non-volatile fraction is commonly referred as char, and it mainly consist of fixed carbon and ash. Another gasification process is char conversion, where the remaining carbon reacts with steam (water-gas reaction Eq. (9)) or oxygen (partial or complete combustion Eq.(2)-(3)). The exothermic combustion reactions are the heat source to drive the endothermic process of pyrolysis and char gasification reactions. Generally, pyrolysis occurs at much higher rates than the gasification reactions.

Depending on the gasifier construction, the exothermic and endothermic reactions can take place in a single reactor vessel or in different vessels. In direct gasifiers (see Figure 3.3), all processes of pyrolysis, char gasification and combustion occurs in one vessel. In the case of using steam, the gasification reactions are endothermic overall. The heat required to drive

those reactions can be supplied externally or by introducing some air into the gasifier to burn part of the available fuel. This second alternative has the inherent disadvantage of diluting the syngas with nitrogen and, hence, lowering its calorific value (~ 5.6-7.5 MJ/Nm^3). Hence, for our calculations, required external heat for the direct steam-blown gasification will be supplied by hot gases released after natural gas burning (see Figure 3.3 case (B)).

Conversely, in indirect gasifiers, pyrolysis and gasification occur in one vessel, and combustion in a separate vessel, i.e., the heat production and consumption process are separated. In this case, a small fraction of char is send to the combustor to produce heat for the gasifier. Unlike direct gasifiers that can use both air and steam, indirect gasifier only use steam as gasifying medium. Examples of indirect gasifiers are the FERCO's SilvaGas process [53] (see Figure 3.4) and the Milena gasifier [54, 55] developed by ECN (see Figure 3.5). Produced syngas has a heating value ~ 13-19 MJ/Nm^3.

The Burlington, Vermont gasifier is the first commercial plant of the SilvaGas indirect gasification process directed by FERCO Industries [53]. This system consists of two separate fluidized beds. The first bed is the gasifier where biomass is converted to gases and a residual amount of char. The unconverted char is then conveyed together with the circulating bed material (sand) to the combustor bed. Heat released during char combustion is absorbed by the circulating sand which is then recycled back to the gasifier bed. The heat transferred from the hot sand is used to maintain the endothermic gasification reactions. The Milena gasifier applies the same principle as the SilvaGas concept, although in this case, the gasifier and the combustor are physically interconnected. Biomass is heated and gasified in a circulating flow of hot sand, and remaining char is send to the combustor. The gasification takes place in a riser, whereas the char combustion and sand heating is done in a fluidized bed.

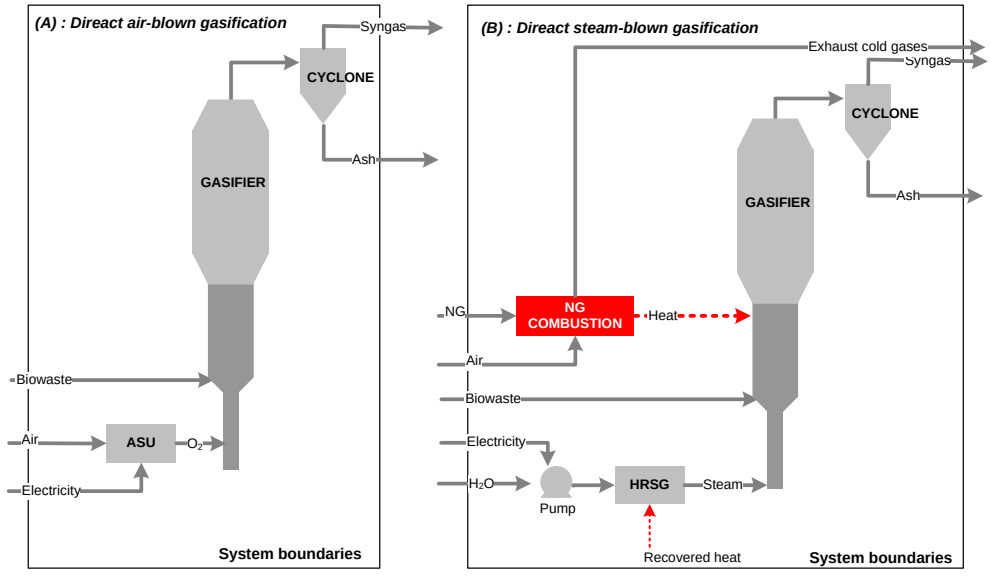


Figure 3.3. Direct gasification using air/oxygen (A) or steam (B) as gasifying medium. In case of steam gasification external heat from natural gas burning is added to the gasifier in order to achieve the desired temperature, i.e., 700^{o}C or above.

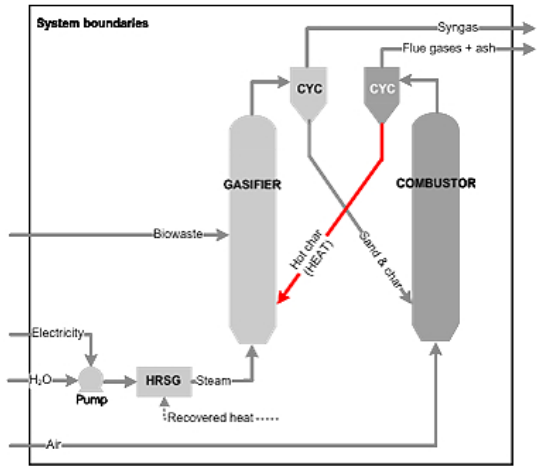


Figure 3.4. Indirect Battelle gasifier system using steam. Heat is provided to the gasifier by means of hot sand from the combustor. This SilvaGas process design belongs to FERCO enterprise [53].

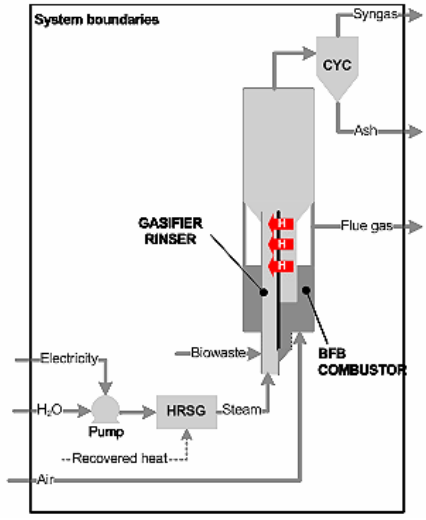


Figure 3.5. Indirect Milena gasifier using steam. Heat (H-arrows) is supplied from the combustor. The design belongs to ECN [54, 55].

Currently, indirect gasification systems are operated near atmospheric pressure. Existing direct gasification systems are more flexible because they can work either under pressurized or at atmospheric pressure. Examples of existing plants are given in section 3.5.

3.4. Gasification Modeling in Aspen Plus

In section 6, the efficiency of biowastes-to-biofuels routes is analyzed based on process models by using Aspen Plus software [56]. The modeling of the gasifier is here explained in detail as it is one of the core operations units of the different routes. The gasifier is modeled in Aspen Plus as two integrated blocks, i.e., a "decomposer" and a gasifier itself. The decomposer is simulated by means of a yield reactor (RYIELD), and this step is required in order to convert the non-conventional biowastes streams for Aspen Plus into the standard constituting components (i.e., carbon, hydrogen, oxygen, sulfur, nitrogen, and ash). This is done by specifying the yield distribution in accordance with the corresponding biomass ultimate and proximate analyses. The heat of formation associated with the decomposition of biomass is connected to the gasifier. A Gibbs reactor (RGIBBS) based on the Gibbs free energy minimization method is used to model the gasifier. This thermodynamic equilibrium method determines the product composition at which the Gibbs free energy of the products reach a minimum, and it takes into account the constraints imposed by the principle of mass and elements conservation (stoichiometry). A key advantage of this method is that it is not necessary to specify the numerous chemical reactions involved during gasification. However, it is necessary to provide a list of all the chemical species that might be present in the gasifier, including reactants and expected products. In case of indirect-steam gasification, the combustor is also simulated as an RGIBBS reactor. Standard Gibbs free energy values of conventional gaseous and liquids components are taken from Aspen Plus thermodynamic databases, but the unconventional solid fraction (char) needs to be approximated to pure carbon graphite. This assumption is quite realistic since typical ultimate analysis reveals that char contains high percentages of carbon, i.e., around 90% [57]. Another assumption that has been taken in our simulations is that the ash is an inert fraction that is not involved in the gasification process.

Moreover, for the case of direct steam-blown gasification, it is assumed that all char is converted to syngas, although this is not always the case in real installations. This assumption has ben adopted in order to determine the best configuration in case of ideal operation. Hence, even if the thermodynamic equilibrium is a rough approximation of the reality, it predicts the maximum achievable yield of desired products and the maximum achievable (theoretical) performance of the gasification system for given process parameters. In fact, when the residence times are long enough, some studies have shown that the inclusion of the solid carbon phase (char) in the model lead to results rather close to experimental data (i.e., errors are usually less than 20%) [58]. The equilibrium approach has also been applied by other authors [58, 59] and results have been compared with experimental data [60-62]. It can be seen that the equilibrium based models give correct orders of magnitude and composition trends. However, under certain conditions, especially at low gasification temperature, the equilibrium model overestimates the yield of H_2 and CO whereas it underestimates the yield of CO_2, CH_4, tars and unconverted char. In fact, under practical conditions in a gasifier, the conversion of tars, methane and char are kinetically limited, and so, they are controlled by

non-equilibrium factors such as chemical kinetics. In particular, tars yield estimation is rather difficult as tars are typically non-equilibrium products which consist of a mixture of polyaromatic hydrocarbons (PAH) and other organic molecules with high molecular weight. In our simulations, it is assumed that tars are assimilated to the solid carbon fraction due to lack of experimental data. Hence, equilibrium based models need to be adjusted for accurate design of specific gasifiers.

3.4.1. Syngas Composition

The effect of the gasifying media, the temperature and pressure on the syngas composition is studied for wood gasification (stream A in Table 3.3). Figure 3.6 depicts the different composition of syngas as a function of temperature and oxidizing agent in direct gasification. Results from air-blown gasifier simulations are not showed here as they followed the same tendency as for oxygen gasification, with the only difference than the product is more diluted with the nitrogen coming from the air. Composition profiles obtained in our Aspen Plus simulations are similar to other authors for two different gasifying media, i.e., steam [61, 63-67] and oxygen (air) [58, 59, 66, 68], although the contents are slightly different. This figure also reveals that steam-blown gasification (dotted lines) yields a higher concentration of H_2, CO, and CH_4, which, in turn, is translated into a higher HHV of the outlet syngas (see Table 3.5). The effect of temperature depends on the gasifying media used. For steam-blown gasification, an increase in temperature is followed by an increase in H_2 and CO content, whereas CO_2, CH_4 and H_2O contents decline. This behavior can be explained by the highly exothermic methanation reactions (7) and (8).

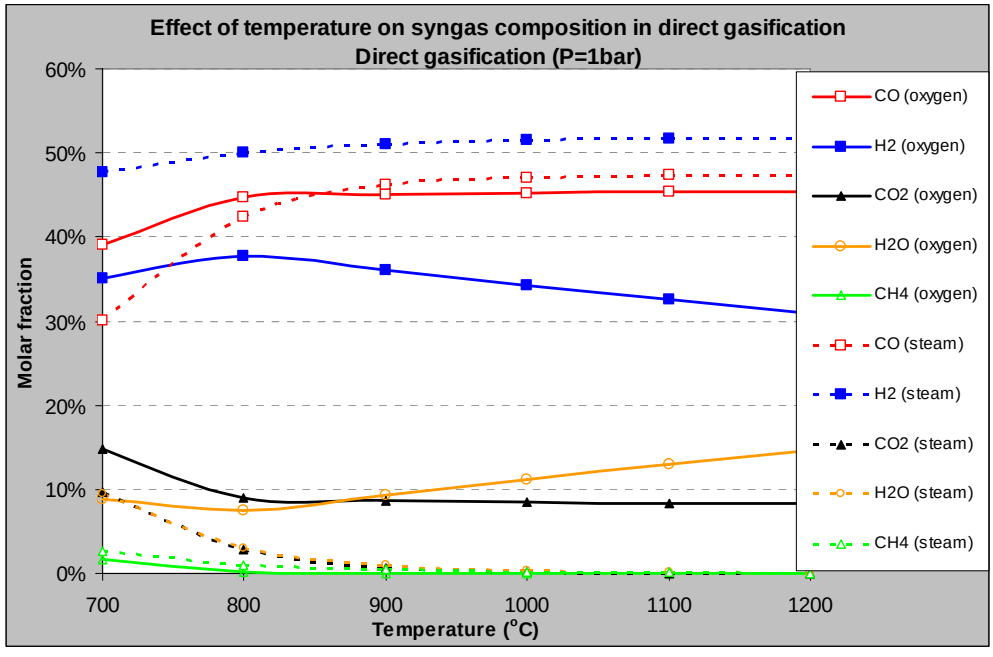


Figure 3.6. Effect of temperature and gasifying media (oxygen and steam) on syngas composition. For the case of steam-gasification (dotted lines) it is assumed that all char is converted to syngas.

Table 3.5. Comparison of HHV of the syngas obtained from the different modes of gasification

Parameters ➡ Operation mode ⬇	700 °C 1 bar	800 °C 1 bar	900 °C 1 bar	1,000 °C 1 bar	1,100 °C 1 bar	1,200 °C 1 bar
Air – direct gasification	6.5	5.9	5.3	4.8	4.3	3.8
O_2 – direct gasification	11.6	13.1	12.7	12.2	11.9	11.5
Steam – direct gasification [(a)]	15.9	18.8	19.8	20.1	20.1	20.2
Steam – indirect gasification	16.0	19.0	20.0	-	-	-
Parameters ➡ Operation mode ⬇	900 °C 1 bar	900 °C 5 bar	900 °C 7 bar	900 °C 10 bar	900 °C 15 bar	900 °C 20 bar
Air – direct gasification	5.3	5.6	5.7	5.6	5.7	5.8
O_2 – direct gasification	12.7	12.8	12.8	12.9	13.0	12.9
Parameters ➡ Operation mode ⬇	700 °C 1 bar	700 °C 5 bar	700 °C 7 bar	700 °C 10 bar	700 °C 15 bar	700 °C 20 bar
Steam – direct gasification [(a)]	15.9	12.9	12.5	12.0	11.6	11.4
Steam – indirect gasification	16.0	13.0	12.5	12.1	-	-

(a) Heat for direct steam-blown gasifiers is supplied from natural gas burning. Char is assumed to be fully converted to syngas.

These reactions are not favored at high temperatures and, hence, less CH_4 and H_2O are formed. Moreover, at high temperatures, less steam is required for the complete carbon conversion. For oxygen-blown gasification (straight lines), the effect of temperature is slightly different. In this case, an increase in temperature causes a clear increase in H_2O, a slight increase in CO content, and a marked decrease in H_2, CH_4 and CO_2 content. This tendency could be justified by Eq.5, as high temperatures favor the reverse reaction towards CO and H_2O formation.

When varying the pressure, the same trend in syngas composition is observed for both oxidizers, i.e., steam and oxygen (see Figure 3.7). These results are also in agreement with previous work of other authors [58]. In case of keeping the same steam flow rate, Puchner et al. found that pressure has no clear effect on CH_4 formation [69]. Higher pressures lead to higher concentration in CH_4, CO_2 and H_2O. In this case, higher methane formation can be explained by methanation Eq. (6)-(8), as these reactions are followed by a decrease in the number of moles (volume).

As observed in the previous figures, if the interest is to produce a syngas rich in methane (e.g. for later SNG production), the preferred conditions are low temperatures, high pressure and steam agent. For other biofuels such as methanol or Fischer-Tropsch fuels, minimization of methane formation is crucial as methane production consumes CO and H_2, the two building agents for alcohols and hydrocarbons formation (Eq.(30)-(34)). Hence, in this case, the preferred conditions would be low pressure, temperature above 800°C and oxygen/air as the gasifying medium. However, the syngas composition alone should not be the decision-maker parameter. Other factors such as efficiency and costs should also be considered.

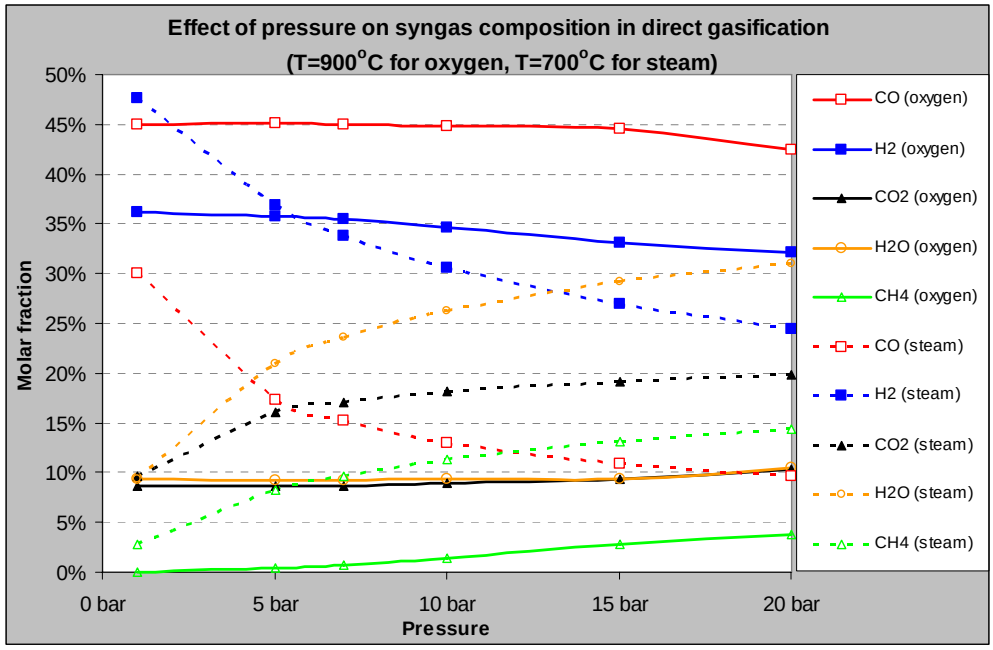


Figure 3.7. Effect of pressure and gasifying media (oxygen and steam) on the syngas composition. Steam gasification is carried out at 700°C, i.e., the temperature where high methane content is achieved. Oxygen gasification is carried out at 900°C, i.e., above the carbon boundary limit, where carbon conversion is complete.

3.4.2. Syngas Calorific Value

When the syngas is used as a fuel itself in internal combustion engines, the optimal gasification conditions are those that yield a product with a higher heating value (HHV). As observed in Table 3.5, steam-blown gasification produces a syngas with higher HHV, especially at high temperatures and low pressures. Values for the direct steam-blown gasification are calculated by considering that all char is converted to syngas, although it may not be the case in real operations.

3.4.3. Gasification Efficiency

The effect of operational parameters such as temperature and pressure on the exergetic efficiency of the gasifier has been analyzed from the results of Aspen Plus simulations. For this analysis, the system boundaries are as shown in Figures 3.3-3.5. Woody wastes (stream A in Table 3.3) dried to 10% moisture content are used for all the cases. Utilities such as air and water are fed at environmental conditions of 25°C and 1 bar. The exit streams are product syngas and separated ash from the cyclones. For the case of steam gasification, hot syngas leaving the gasifier is used to produce steam from cold water, and the heat required to run the gasifier is supplied by either unconverted char combustion (indirect gasification) or by natural gas burning (direct gasification). For this last process, natural gas burning provides heat with a gradient temperature of 200°C, and the remaining heat is used to produce surplus steam. The exergetic efficiency of natural gas burning is around 55-59%, and it has been included in

the calculations. Equations (11-12) are used to calculate the exergetic efficiency of air and oxygen-blown gasifiers working above the carbon boundary point.

$$\Psi_{ex,air\ gasifier} = \frac{E_{syngas} + E_{ash}}{E_{dried\ wood} + W_{in,compressor}} \tag{11}$$

$$\Psi_{ex,oxygen\ gasifier} = \frac{E_{syngas} + E_{ash}}{E_{dried\ wood} + W_{in,compressor} + W_{in,ASU}} \tag{12}$$

where E_{syngas}, E_{ash}, $E_{dried\ wood}$ refers to the exergy of syngas, ash and woody streams, whereas $W_{in,compressor}$ and $W_{in,ASU}$ is the power consumed by the compressors and the air separation unit (ASU), respectively. In order to convert all carbon at temperatures below the carbon boundary point (see Figure 3.10), heat has to be removed as the addition of stoichiometric amount of air (or oxygen) would increase the gasifier temperature. In that case, exergy of the removed heat (E_{out}^{Q}) is added to the numerator of Eqs.(11-12). Equations (13-14) apply for the case of indirect and direct steam blown-gasifiers.

$$\Psi_{ex,indirect\,steam\text{-}gasifier} = \frac{E_{syngas} + E_{ash}}{E_{dried\ wood} + W_{in,pump} + E_{H_2O,liq}} \tag{13}$$

$$\Psi_{ex,direct\,steam\text{-}gasifier} = \frac{E_{syngas} + E_{ash} + E_{steam}}{E_{dried\ wood} + W_{in,pump} + E_{H_2O,liq} + E_{NG}} \tag{14}$$

where $E_{H2O,liq}$ is the exergy on inlet water at 25°C and 1 bar, E_{NG} is the exergy of natural gas that is burned to provide heat for the gasifier, and E_{steam} is the exergy of steam produced from exhaust gases of the natural gas burning process.

3.4.4. Effect of Temperature and Gasifying Agent

Temperature is the primary parameter tested for the gasification efficiency. For this analysis, the pressure of the gasifier has been kept constant at 1 bar and different gasifying mediums have been used, i.e., air, oxygen and steam. Results are shown in Figure 3.8. As observed, high temperatures have a negative effect on the exergetic efficiency of the gasifier. This statement is valid for the case that all carbon is being converted (except for the case of steam-blown indirect gasification) although this might not be always the case in real installations. For the simulations of direct gasification, the amount of air or steam added to the gasifier is adjusted to reach complete carbon conversion. For indirect gasification, less steam is required as only partial carbon conversion occurs. The amount of unconverted carbon that is later combusted in a separated reactor is adjusted to fulfill the heat demand of the gasifier, as shown in Figure 3.9. As expected, the exergetic efficiency is negatively affected when increasing the amount of unconverted char. However, at temperature above 850°C, it is found that less steam to gasify the char and, hence, exit streams have notably a higher temperature (higher physical exergy).

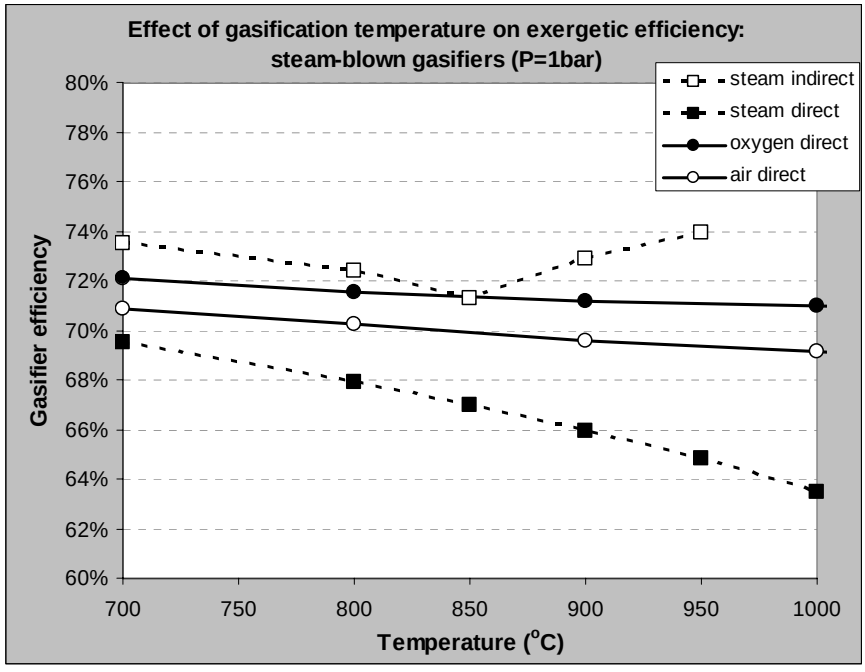


Figure 3.8. Effect of the gasification temperature on the exergetic efficiency of the gasifier. Comparison of direct gasification using air, oxygen and steam as blasts, and indirect gasification using steam.

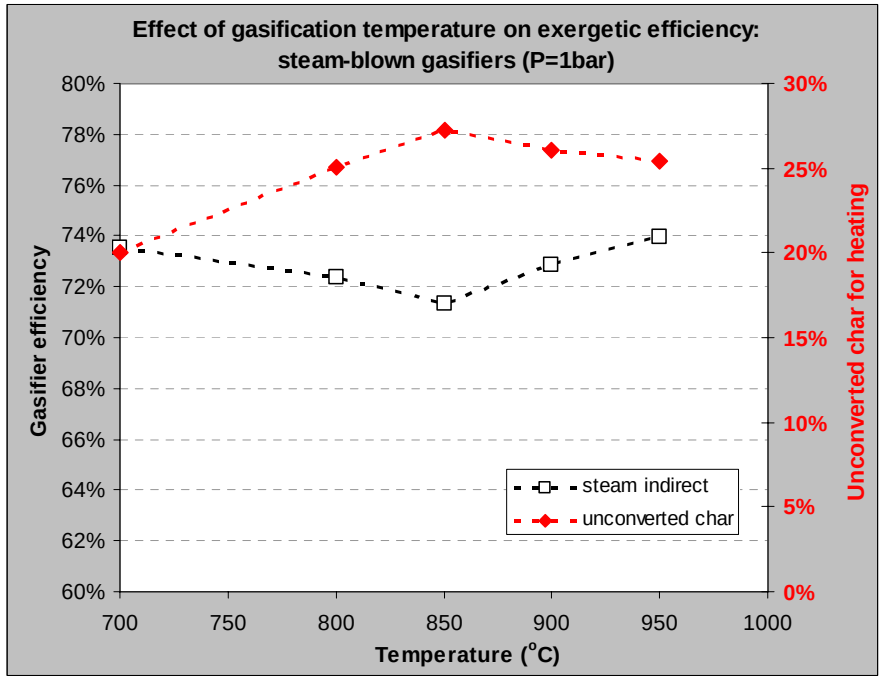


Figure 3.9. Effect of temperature on the unconverted char required for heating the gasifier. Exergetic efficiency is directly affected by this parameter.

On the other hand, if the amount of steam is kept constant, higher efficiencies are expected at higher temperatures as more carbon will be converted [58, 70].

3.4.5. Effect of Pressure and Gasifying Agent

The effect of pressure and the corresponding efficiencies have also been studied for the 3 gasifying mediums, i.e., air, oxygen and steam, and for direct and indirect gasification in the case of steam. Energy required for the ASU unit has also been taken into account. For the case of direct gasification with air and oxygen, highest efficiencies are expected near the carbon boundary point, i.e., when all carbon is converted [71]. Figure 3.10 shows the carbon boundary point in function of the gasification pressure.

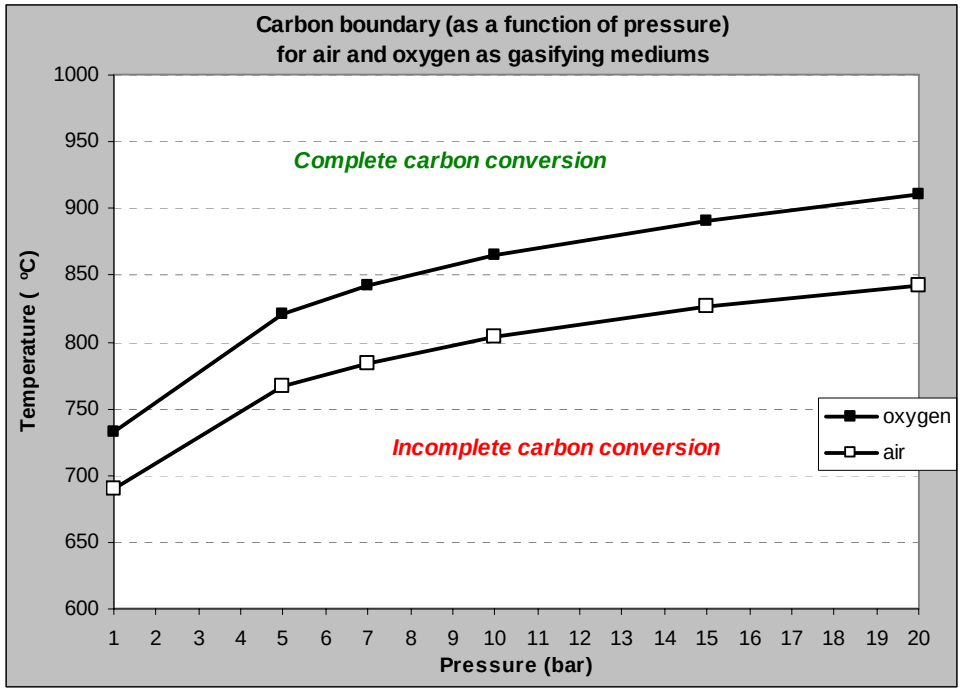


Figure 3.10. Carbon boundary point of wood gasification as function of pressure.

The effect of pressure on the exergetic efficiency of the gasifier is different when working below or above the carbon boundary point, as shown in Figure 3.11 and Figure 3.12. Higher efficiencies are obtained at higher pressures when the analysis is conducted at a temperature above the carbon boundary, i.e., 900°C. The opposite tendency is observed when working below the carbon boundary, i.e., 700°C. In all cases, complete carbon conversion occurs, but in the case of 700°C, heat must be removed from the gasifier to attain the desired temperature.

The same analysis has been conducted for steam-blown gasification in either indirect or direct mode at 700°C. Results are presented in Figure 3.13. As for the case of air and oxygen gasification, high pressures have a positive influence on the exergetic efficiency of the gasifier. This could be explained by the fact that more methane is produced, which, in turn,

has a higher chemical exergy. Moreover, at high pressure, less unconverted char is required for heating the gasifier (see Figure 3.14).

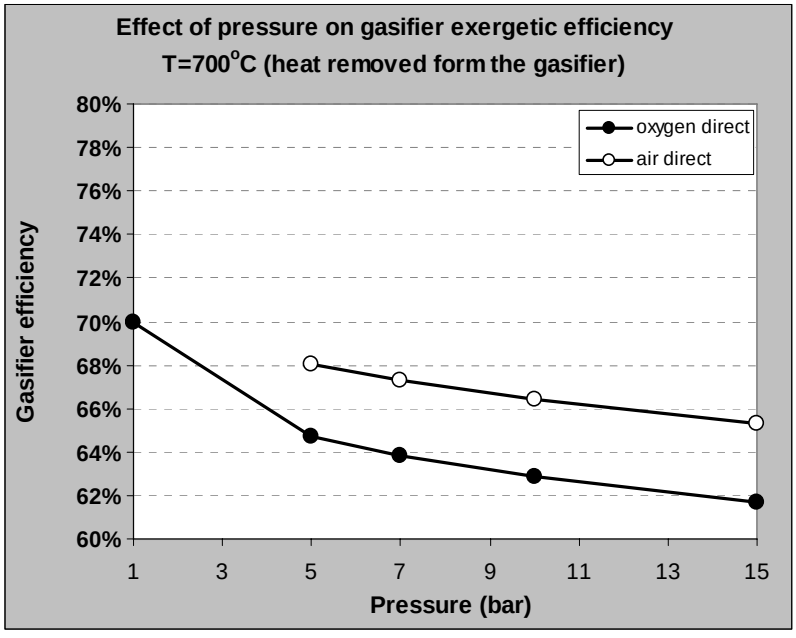


Figure 3.11. Effect of pressure when using air and oxygen in direct gasification, at a constant temperature of 700°C. Heat is removed to achieve complete carbon conversion.

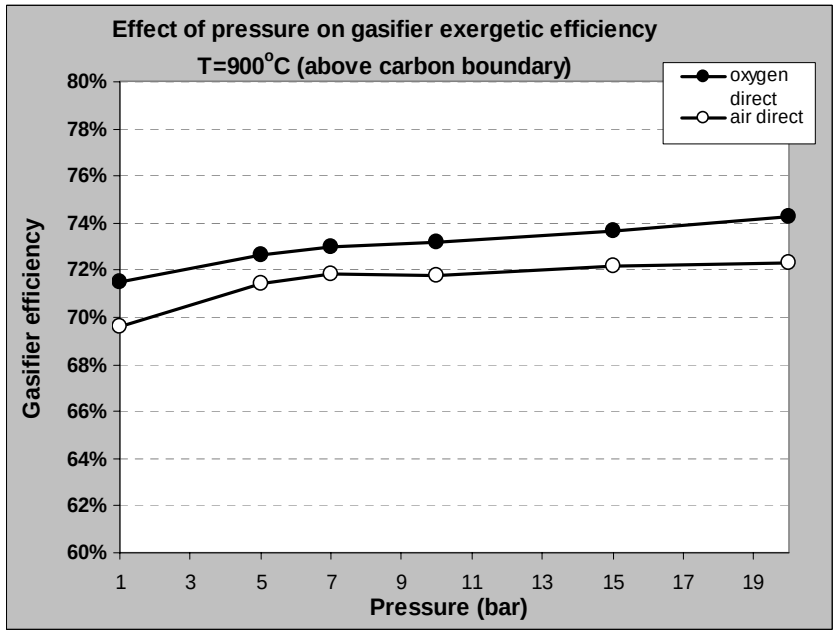


Figure 3.12. Effect of pressure when using air and oxygen in direct gasification, at a constant temperature of 900°C (i.e., above carbon boundary temperature).

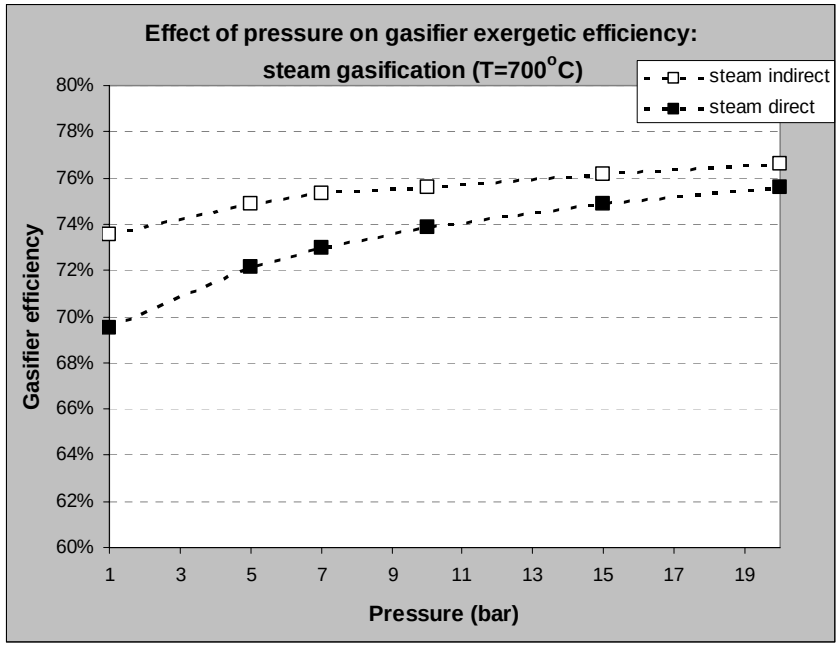


Figure 3.13. Effect of pressure when using steam as gasifying medium in indirect and direct gasification, at 700°C.

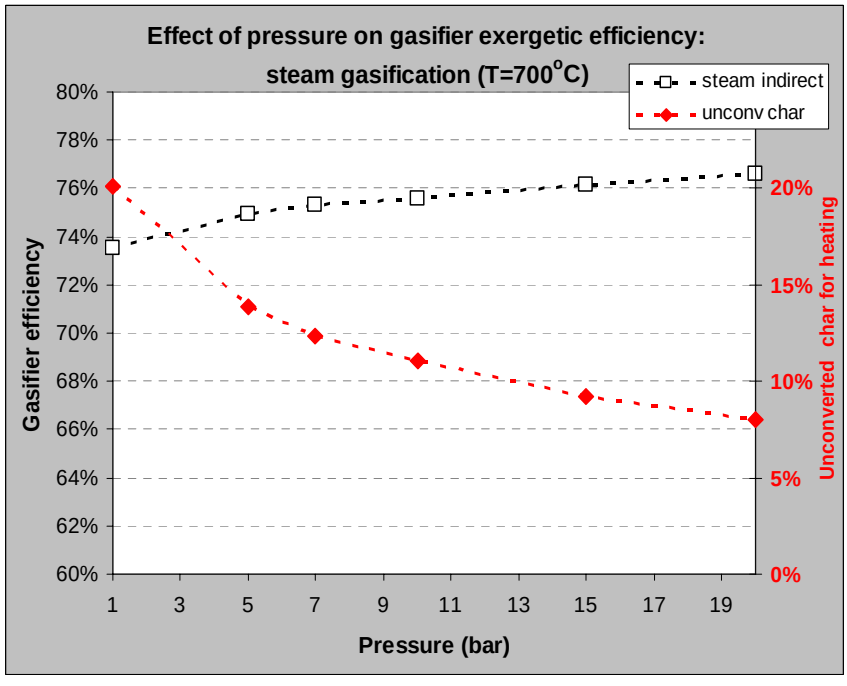


Figure 3.14. Effect of pressure on the unconverted char required for heating the gasifier. Exergetic efficiency is directly affected.

Table 3.6. Overview of several gasification plants and pilot plants within Europe

Location	Project name and Supplier	Process description	Capacity (input)	Production (output)	Feedstock	Status	Biofuels production
Güssing (Austria)	BIO-SNG	FICFB: Fast Internal Circulation Fluidized Bed, i.e.: 2 fluidized bed: gasifier + combustor separated. Steam as gasifying agent	-	1 MW of SNG	Wood chips	Demonstration plant ready by 2008	SNG
Güssing (Austria)	BIO-FIT (Renew EU project)	FICFB: Fast Internal Circulation Fluidized Bed, i.e.: 2 fluidized bed: gasifier + combustor separated. Steam as gasifying agent	-	-	Wood chips	Pilot plant running since 2005	Fischer-Tropsch
Güssing (Austria)	AER-GAS	FICFB: Fast Internal Circulation Fluidized Bed, i.e.: 2 fluidized bed: gasifier + combustor separated. Steam as gasifying agent	-	100 kW	Wood chips	Laboratory scale since 2006 Production will be tested in the existing 8MW Gussing plant in Austria.	Hydrogen
Güssing (Austria)	CHP plant Supplier: Repotec	FICFB: Fast Internal Circulation Fluidized Bed, i.e.: 2 fluidized bed: gasifier + combustor separated. Steam as oxidizing agent	2.2 tph (= 8MW)	2 Mwe + 4.5 MWth	Wood chips	Demonstration plant in operation since 2001	Heat and Electricity
Zeltweg (Austria)	BioCoComb Thermie program Supplier: Hydro Power	CFB: Circulating Fluidized Bed Co-combustion with coal Air as gasifying agent	10 MWth	Globally, 137 Mwe	Coal and wood chips, bark, sawdust.	Plant in operation since 1998	Heat and Electricity
Wiener Neustadt (Austria)	Wiener Neustadt	FICFB: Fast Internal Circulation Fluidized Bed Air as gasifying agent	2 MWth	0.5 Mwe + 0.7 MWth	Wood	Plant in operation since 2000.Plant commission in 2003	Heat and Electricity
Pols (Austria)	Pols Bark gasifier project	Lurgi CFB: Circulating Fluidized Bed gasifier Air as gasifying agent	6.6 tph (= 35MW)	-	Wastes from a paper mill	Plant erected in 1987. It has been only used for tests	Heat and Electricity

Table 3.6 (Continued)

Location	Project name and Supplier	Process description	Capacity (input)	Production (output)	Feedstock	Status	Biofuels production
Ruien (Belgium)	Ruien project and supplier: Foster Wheeler	CFB: Circulating Fluidized Bed Co-combustion with coal Air as gasifying agent	50 MWth	Globally, 250MWe	Coal and wood chips	Plant in operation since 2003	Heat and Electricity
Seco-Bois (Belgium)	Supplier: Xylowatt SA	Down-draft gasifier Air as gasifying agent	-	0.6 MWe	Wood chips	Plant under commission	Heat and Electricity
Gedinne (Belgium)	Supplier: Xylowatt SA	Down-draft gasifier Air as gasifying agent	-	0.6 MWe	Wood chips	Plant under commission	Heat and Electricity
Louvain (Belgium)	SRC-Gazel Supplier: Universite Louvain	Down-draft gasifier Air as gasifying agent	0.50 MWth	0.15 MWe	Wood chips, short rotation coppice	Pilot plant in operation by 1998 (1000 hours in operation)	Heat and Electricity
Harboore (Denmark)	Harboore project Supplier: Ansaldo Volund Energy	Up-draft gasifier Air as gasifying agent	3.5 MWth	1 MWe + 2 MWth	Wood wastes	Plant in operation since 1996. Power production since 2000	Heat and Electricity
Hogild (Denmark)	Holgid project Supplier: Hollesen Engineering Company	Down-draft gasifier Air as gasifying agent	0.5 MWth	$\eta_{electricity}$: 24%	Clean wood and wood wastes, sawdust	In operation since 1998	Heat
Skive (Denmark)	Carbona CHP project Suppliere: Carbona	BFB: Bubbling Fluidized Bed (Renugas type) Air as gasifying agent	30,000 tpy (=30MW_{th})	5.5 MWe + 11.5 MWth	Biomass	Plant construction by 2005 Plant comission by 2006	Heat and Electricity
Graested (Denmark)	Castor plant project Supplier: Biosynergi	Down-draft gasifier Air as gasifying agent	Nowadays: 400 kWth	Nowadays: 90 KWe + heat Future: 0.25 – 1 MWe	Wood pellets, wood chips, wood wastes	Demonstration plant erection by 2003. Tests running since 2004. Plans to scale-up	Heat and Electricity
Blære, Aars	Blære project Supplier: REKA	2 stage gasification process (pyrolisis+gasifier)	400 kWth	20 kWth + 100 kWe	Biomass	Pilot plant, 100 hours in operation	Heat and Electricity

Location	Project name and Supplier	Process description	Capacity (input)	Production (output)	Feedstock	Status	Biofuels production
(Denmark)		Steam/air as gasifying agent					
Gjoel (Denmark)	Gjoel Project Supplier: TK Energi AS	2 stage gasification process (pyrolisis+gasifier) Air as gasifying agent	2,3 MWth	0.9 MWth + 0.5 MWe	Wood wastes, wood chips	Construction plant by 2005 Hot test running since 2006	Heat and Electricity
Tampere (Finland)	Enviropower pilot plant Supplier: Carbona Oy	Pressurized CFB: Circulating Fluidized Bed Air/steam as gasifying agent	15 MWth	15 MWth	Waste wood	Plant in operation since 1991	Heat and Electricity (IGCC)
Hameenlinna (Finland)	Supplier: Foster Wheeler Energia Oy	Bioneer updraft gasifier Air as gasifying agent	-	1.5 MWth	Wood	Plant in operation since 1985	Heat
Ilomantsi (Finland)	Supplier: Foster Wheeler Energia Oy	Bioneer updraft gasifier Air as gasifying agent	-	6.4 MWth	Wood chips	Plant in operation since 1996 8000 hours in operation	Heat
Kaukajoki (Finland)	Supplier: Foster Wheeler Energia Oy	Bioneer updraft gasifier Air as gasifying agent	-	5 MWth	Wood chips	Plant in operation since 1985 8000 hours in operation	Heat
Lahti (Finland)	Supplier: Foster Wheeler Energia Oy	Pressurized CFB: Circulating Fluidized Bed Air as gasifying agent	18 tph (40-70 MWth)	167 MWe + 240 MWth	Clean and wood wastes, sawdust, MSW, short rotation coppice	Operational since 1998, upgrading gas cleaning	Heat and Electricity
Varkaus (Finland)	Supplier: Corenso and Foster Wheeler Energia Oy	CFB: Circulating Fluidized Bed Air as gasifying agent	-	40 MWth	packaging wastes from wood fibres, aluminium, plastic	Scale-up from a 15 MW pilot plant. Commission by 2000	Heat
France	Raud project Supplier: Martezo	Down-draft gasifier Air as gasifying agent	-	0.1 MWe	Wood	Plant start-up in 1983	Electricity

Table 3.6 (Continued)

Location	Project name and Supplier	Process description	Capacity (input)	Production (output)	Feedstock	Status	Biofuels production
Rudersdorf (Germany)	Rudersdorf Zement Supplier: Lurgi technology	CFB: Circulating Fluidized Bed Air as gasifying agent	100 MWth	80 MWth	Demolition wood	Plant in operation since 1996. By 2000, it was the largest installed biomass gasifier	Heat
Domsland (Germany)	BEV-Domsland AHT Pyrogas Vertriebs GmbH	Down-draft gasifier Air as gasifying agent	-	0.18 MWe	wood, demolition wood, wood chips	Plant in operation since 2000	Electricity
Clausthal- (Germany)	EU project: FPG-502705	BFB: Bubbling Fluidized Bed Cutec pilot plant Air/O_2/steam gasifying agents	-	0.4 MWth	Wood, straws, industrial crops	Pilot plant scale since 1995	Fischer-Tropsch fuels
Lausitz (Germany)	SVZ Schwarze Pumpe GmbH	5 fixed beds + 1 entrained flow gasifier	120,000 tpy (=130 MWth)	75 MWe	Coal, RDF, plastics, wood chips, sludge	Commercial plant since 1995	Methanol, Heat, and Electricity
Freiberg (Germany)	Alpha plant-SunFuel Supplier: CHOREN	3 stage gasifier Air/O_2/steam gasifying agents	1 MW	1 MW	Biomass	17,000 operation hours since pilot plant in 1994	Fischer-Tropsch, heat, electricity
Freiberg (Germany)	Beta plant-SunFuel Supplier: CHOREN	3 stage gasifier Air/O_2/steam gasifying agents	75,000 tpy (=45 MWth)	16.5 million lts of Sunfuel	Biomass	Plant completion by 2006-2007	Fischer-Tropsch, heat, electricity
Freiberg (Germany)	Sigma plant-SunFuel Supplier: CHOREN	3 stage gasifier Air/O_2/steam gasifying agents	1,000,000 tpy (=600 MWth)	200,000 tpy of Sunfuel	Biomass	Plant completion by 2008-2009	Fischer-Tropsch, heat, electricity
Greve in Chianti (Italy)	Chianti project Supplier: TPS	CFB: Circulating Fluidized Bed Air as gasifying agent	2 x 100 tpy (=15 MWth)	6,7 MWe	RDF	Commercial plant by 1993	Heat and Electricity

Location	Project name and Supplier	Process description	Capacity (input)	Production (output)	Feedstock	Status	Biofuels production
Cascina,Pisa (Italy)	Bioelettrica project Thermie Energy Farm	Air blown gasifier	43 MWth	14 MWe	Wood, agriculture wastes	Start-up plant by 2002 Plant shutdown	Heat and Electricity
Rossano (Italy)	Rossano Calabro project, PRM	Up-draft gasifier Air as gasifying agent	-	4.5 MW_e	Olive pits	Plant under commission	Electricity
Petten (Netherlands)	Milena Project ECN	Indirect gasifier, steam as gasifying agent	25 MW	-	Wood chips	Laboratory scale plant	SNG
La Coruña (Spain)	La Coruña project, Guascor technology	Updraft gasifier, Co-combustion Air as gasifying agent	9 tpd	1 MWe	Waste tyres	Plant in operation since 2000	Heat and Electricity
Mora d'Ébre (Spain)	Energia Natural de Mora	Fixed bed Air as gasifying agent	-	0.5 MWe $\eta_{electricity}$:30 % $\eta_{thermal}$:40%	Almond shells, wood chips, demolition wood bagasse, GFT, and more	Plant in operation since 1997, 20,000 hours in operation	Heat and Electricity
Ribesalles (Spain)	Poligas plant EIE SL, Poligas	Fixed bed Air as gasifying agent	-	-	Biomass wastes	Star-up plant by 2002. Plant shut-down by 2004	Heat and Electricity
Rya (Sweden)	GobiGas project	Steam gasification + Methanation stages	-	11Mm^3 SNG per year	Forestry residues	Plant in operation by 2010. Currently, research ongoing	SNG
Värnamo (Sweden)	IGCC Värnamo, Bioflow (Skydraft, Foster Wheeler)	CFB: Circulating Fluidized Bed Air as gasifying agent 1st IGCC plant with wood	4 tph (=18 MWth)	6 MWe + 9 MWth	Wood, forestry, bark, sawdust, RDF	Construction by 1991-1993 Plant in operation 1993-1999 Mothballed in 1999, Plant rebuilt for Chrisgas project	Heat and Electricity (IGCC)

Table 3.6 (Continued)

Location	Project name and Supplier	Process description	Capacity (input)	Production (output)	Feedstock	Status	Biofuels production
Värnamo (Sweden)	Chrisgas	CFB: Circulating Fluidized Bed Steam as gasifying agent	3.5 tph (=18 MWth)	7000 Nm3/hr of syngas	Wood, forestry, bark, sawdust, RDF	Project start by 2003 Pilot plant by 2008	Hydrogen, DME and methanol
Trollhatan (Sweden)	BioMeet project	Research ongoing	229 MW	550 tpd of methanol	Forest, wood and agriculture wastes	Research ongoing	Methanol
Norrsundet (Sweden)	Foster Wheeler Energia Oy	CFB: Circulating Fluidized Bed Air as gasifying agent	27 MWth	20 MWth	Wood, bark	Plant in operation since 1985	Heat
Lid (Sweden)	Foster Wheeler Energia Oy	Updraft gasifier Air as gasifying agent	10 MWth	-	Wood chips, bark	Plant in operation since 1986	Heat
Karlsborg (Sweden)	Foster Wheeler Energia Oy	Updraft gasifier Air as gasifying agent	25 MWth	-	Wood chips, bark	Plant in operation since 1985	Heat
Varo (Sweden)	Kvaerner Pulping AB	CFB: Circulating Fluidized Bed Air as gasifying agent	35 MWth	-	Wood chips, bark	Plant in operation since 1987	Heat
Frovifors (Sweden)	Kvaerner Pulping AB	CFB: Circulating Fluidized Bed Air as gasifying agent	4 MWth	-	Wood chips, bark	Plant in operation since 1993	Heat
Pitea (Sweden)	Chemrec	EF: Entrained Flow Air as gasifying agent	0.5 MWth	-	Wood chips, bark	Pilot plant by 1994	Heat
Spiez (Switzerland)	Pyroforce gasifier, KHD technology	Down-draft gasifier Air as gasifying agent	-	0.2 MWe	Cleand and wood wastes	Plant commission by 2001 Plant in operation since 2002	Heat and Electricity
Yorkshire (UK)	ARBRE project TPS technology	TPS atmospheric gasifier Air as gasifying agent	43,000 tph	8 MWe	Wood	Construction by 1998, but Plant shutdown after 2000	Heat and Electricity

Location	Project name and Supplier	Process description	Capacity (input)	Production (output)	Feedstock	Status	Biofuels production
Blackwater Valley-Ireland	Exus Energy	Down draft gasifier Air as gasifying agent -	-	0.2 MW_e	Biomass	In operation, 1.000 hrs operating	Heat and Electricity

3.5. State-of-the-Art of Gasification

Coal gasification has been successfully applied on a commercial scale worldwide for more than 50 years in the refining, fertilizer, and chemical industries, and for more than 35 years in the power industry. Concerns about the harmful effects of using coal have motivated the research and development of new biomass gasification plants. However, there are considerably less commercial plants that partially or fully run on biomass or wastes feedstocks. For instance, in the Netherlands, biomass is just co-fired in 8 out of 25 existing gasification plants. In total, nowadays, there are more than 140 gasification plants in operation around the world that convert different organic sources from coal to biomass. Worldwide gasification technology is expected to grow 70% by 2015, with 80% of the growth occurring in Asia. The prime movers behind this expected growth are the chemical, fertilizer, and coal-to-liquids industries in China, oil sands in Canada, polygeneration (hydrogen and power or chemicals) and SNG in the United States, and refining in Europe (Gasification Technologies Council). Figures about biomass gasification are less clear but there is a growing interest in this technology. Table 3.6 presents some examples of biomass gasification systems operating in Europe and using different biomass and wastes feedstocks.

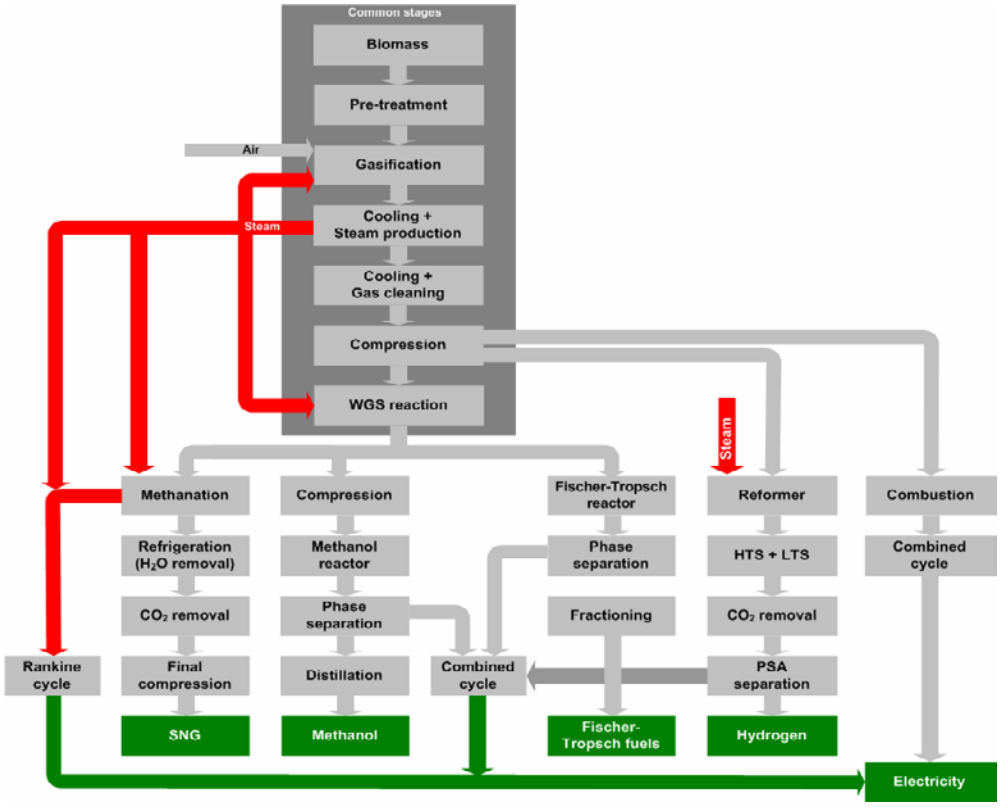


Figure 4.1. Overview of the 5 biowaste-to-biofuel conversion routes.

4. TECHNOLOGY SELECTION FOR BIOFUELS PRODUCTION

In this section, the efficiency analysis is presented for various biofuels, i.e., SNG, methanol, Fischer-Tropsch fuels, hydrogen and heat-electricity. Heat and electricity are co-produced and consumed in all the processes reducing the need of external fuel. In some cases, however, external fuel is still needed to cover the overall energy demand. Figure 4.1 schematically shows the main stages of each route.

These 5 production chains have been modeled in Aspen Plus [56] and mass and energy balances obtained from the simulations are used for later energy efficiency and exergy analysis. Table 4.1 presents the operational conditions of the main units of each process.

Table 4.1. Comparison of the main operational parameters for the production of the 5 biofuels

Section	Parameter	SNG	Methanol	F-T fuels	Hydrogen	Electricity
Drying	Final MC Temperature (out)	10% 115 °C	10% 115 °C	10% 115 °C	10% 115 °C	10% 115 °C
Gasifier	Pressure Temperature Heating Gasifying agent	1 bar 700 °C Indirect Steam	1 bar 900 °C Direct Air	1 bar 900 °C Direct Air	1 bar 700 °C Indirect Steam	1 bar 900 °C Direct Air
Cleaning: CO_2 and H_2S removal	T - feed T - solvent T - regeneration P- absorber P- stripper Solvent	55 °C 40 °C 105-110 °C 1 bar 2 bar MDEA	55 °C 40 °C 105-110 °C 1 bar 2 bar MDEA	55 °C 40 °C 105-110 °C 1 bar 2 bar MDEA	55 °C 40 °C 105-110 °C 1 bar 2 bar MDEA	55 °C 40 °C 105-110 °C 1 bar 2 bar MDEA
Cleaning: NH_3 removal	Temperature Pressure Solvent	40 °C 1 bar H_2SO_4	40 °C 1 bar H_2SO_4	40 °C 1 bar H_2SO_4	40 °C 1 bar H_2SO_4	40 °C 1 bar H_2SO_4
WGS reactor or Reformer*	Pressure Temperature Catalyst H_2: CO ratio	28 bar 398°C Ni-based 3	25 bar 330°C Cu/Al_2O_3 2	25 bar 330°C Cu/Al_2O_3 2.13	* 35 bar * 850°C *Ni-based -	- - - -
Catalytic reactors	Name No reactors Pressure Temperature Catalyst	Methanation 4 28 bar 398-300 °C Ni-based	Methanol reactor 1 77 bar 200 °C Cu/Zn/Al	F-T reactor 1 23 bar 260 °C Co-based	HTS and LTS HTS:1 LTS:1 HTS: 30 bar LTS: 25 bar HTS: 435 °C LTS: 220 °C Fe_3O_4-Cr_2O_3 ZnO-CuO	- - - - -
Upgrading	Final stages	H_2O removal CO_2 removal Compression	Phase separation Distillation	Distillation Fractioning	CO_2 removal PSA separation	Combined cycle
Final product	Specification	Wobbe index: 43.5 MJ/Nm^3	Methanol purity: ≤ 98.6 %	Linear hydrocarbons	H_2 purity: 99 %	-

4.1. System Boundaries

Figure 4.2. schematically shows the system boundaries conditions for all conversion routes, where the main conditions are as follows:

- Utilities such as processing water and air are supplied at 25°C and 1 bar, which are the same environmental conditions adopted for the exergy analysis. Steam is produced in the plant.
- Chemicals such as MDEA and H_2SO_4 are supplied at 40°C and 1 bar.
- Heat demand in case of indirect gasification (SNG and Hydrogen chains) is supplied by burning unconverted char. Hence, external heat supply is not required in this case
- Heat required for the boilers of the stripping columns (H_2S and CO_2 removal in amines absorption system) has to be supplied externally. Heat required for the rest of the units is covered by heat recovery within the plant.
- Logistics costs has not been included yet. Hence, the current analysis considers that biowastes are delivered on-site.
- Waste water and exhaust gas treatment is not included in the current analysis.

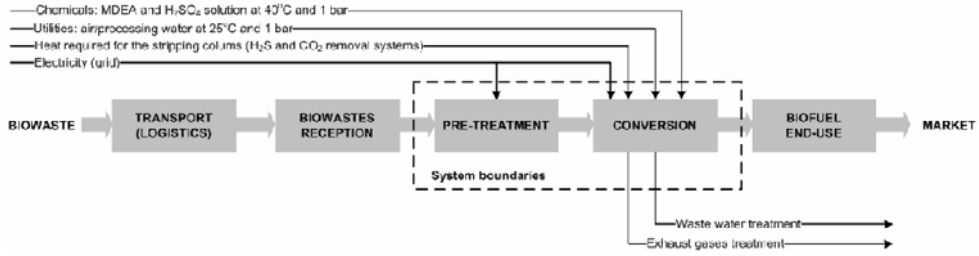


Figure 4.2. System boundaries for the exergy analysis and later economic and environmental impact analysis.

4.2. Pre-Treatment

Pre-treatment stages are required in order to convert biowastes into a feedstock more effectively to storage, handle and process. Generally, pre-treatment operations include biowastes reception, size reduction, drying and densification. However, the required operations and their extension ultimately depend on the selected biowaste as well as on the specific requirements of the gasifier and its feeding systems. The gasifier type (fixed, fluidized or entrained bed) especially determines the required degree of size reduction as this reactor is designed for a particular residence time, which is again governed by the particle size (see Table 4.4). Moreover, due to the short residence times of the reactors (especially for fluidized and entrained beds) fuel size distribution should also be as much uniform as possible.

Another parameter that notably influences the gasifier performance is the moisture content of the biowaste. Several studies state that higher gasification efficiencies are expected when the inlet biowaste stream is dried up to 10-20% [51]. Densification practices such as

pelletizing, briquetting and more recently torrefaction, increase the bulk density and reliability of the feed, and, in turn, the gasifier efficiency [72, 73]. Figure 4.3 summarizes the pre-treatment stages applied to each biowastes, and next sections 4.2.1 to 4.2.7 gives more information.

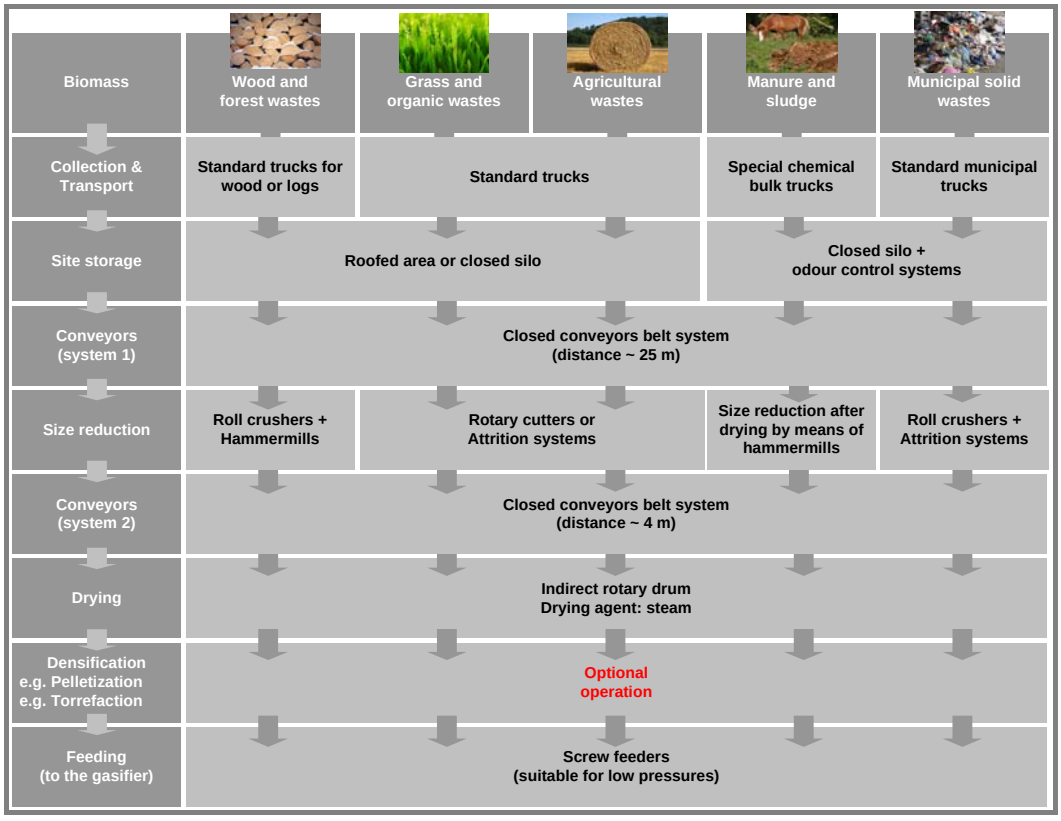


Figure 4.3. Main pre-treatment stages for five different biowastes.

4.2.1. Reception

Truck scales and transshipment devices (e.g., cranes, shovels or hoists) are incorporated for the reception of biowastes in the processing plant. Trucks scales and transshipment are simulated in Aspen Icarus to determine investment and operational costs and results are also compared with literature data [51]. Energy consumption of transshipment devices, in particular cranes, are estimated to be 2.32 MJ/m^3 [51].

4.2.2. Storage

Storage is normally required to assure continuous operation of any plant, and the corresponding facility type directly depends on the properties of the biowaste. Storage can be done in the open air, in a roofed shelter, inside a building, in a silo or even in a bunker, and with or without ventilation and odor control systems. In our case, all biowastes are assumed to be stored in silos, even though material such as wood could also be piled up in open air with lower investment costs. An active removal system (such as screw discharges) can also be incorporated in order to avoid biowastes agglomeration and assure an uniform discharge.

The required storage facility capacity is calculated by considering 1 day of autonomy, i.e., the equivalent fresh biowaste amount for continuously running the plant during 24 hours. Larger periods are not envisaged in order to avoid severe biological degradation of biowastes containing more than 20% of moisture content. This would be the case of all the biowastes streams considered here except for the woody wastes (see Table 2.3).

4.2.3. Conveying Systems

Biowastes need to be transported among storage facilities, other pre-treatment equipments and the gasifier section. Due to their versatility, reliability and reasonable costs, closed belt conveyors are selected for all the biowastes streams, assuming a speed of 2-5 m/s and a belt width of 600 mm. Conveyors are simulated in Aspen Icarus [74] as DCO-CLOSED-BLT type, and results are used for later cost analysis. Electricity consumption for later presented efficiency analysis is calculated from the following relation [75]:

$$W = 0.00058 \cdot m_i^{0.82} \cdot L \tag{15}$$

where W is the power (in Hp), m_i is the mass flow rate (in lb/s) and L is the length (in ft).

4.2.4. Size Reduction

Particles size of biowastes streams are adjusted to meet the requirement of the feeding system and the gasifier. Basically, there are three types of sizing equipments, i.e., crushers or impact mills, shredders and cutters. Four our case, the desired final particle size is 4 mm, and the corresponding selected equipments are listed in previously mentioned Figure 4.3. Roll crushers are firstly used for wood and municipal solid waste streams to crush materials into a smaller size which can be further reduced by means of a hammer mill and attrition systems respectively. Rotary cutters are preferred for fibrous materials such as grass and agricultural wastes, as successive shear actions are more effective than pressure or physical impact. The features of each equipment are presented in Table 4.2 whereas required specifications are tabulated in subsequent Table 4.3, and electricity consumption is calculated from Eq. (16-18).

$$W = 0.3 \cdot m_i \cdot R^* \tag{16}$$

$$W = 500 \cdot m_i \tag{17}$$

$$W = 40 \cdot m_i \cdot \ln\left(R^*\right) \tag{18}$$

where W is the power (in Hp), m_i is the mass flow rate (in lb/s) and R^* is the reduction ratio.

4.2.5.Drying

Prior to gasification, all biowastes streams are dried to 10% of moisture content. There are several devices available in the market but in our case a rotary indirect drum dryer is selected. Rotary drum drying is the most simple and well proven technology for biomass applications [51]. The selected dryer is built in a completely closed system to prevent odor

and hazard problems, although the corresponding investments costs are higher than traditional direct open systems. Indirect dryers are characterized by the transfer of heat to the biowaste through a retaining wall. The drum is rotated in order to facilitate mass and heat transfer. In our case, hot gases or steam produced within the plants are used to evaporate the water at 115^{o}C and 1 bar. The evaporated water is removed independently of the heating medium. The rotary indirect drum dryer is simulated in Aspen Icarus using the *INDIRECT* module. Specific electricity production is taken from Pierik et al [51] for an indirect rotary drier, i.e., 15 kWh per ton of wet material and it is calculated for each biowaste stream.

Table 4.2. Comparison of different size reduction equipments

Equipment	Simulated in [74] as:	Capacity	Reduction ratio (R*)	Electricity consumption
Roll crusher	CR-S-ROLL-MED	max. 1,330tn/hr	max. 16	Eq.(16)
Rotary cutter	Data taken from	max. 180tn/hr	max. 10	Eq.(17)
Hammer mills	CR-REV-HAMR	max. 408tn/hr	max. 50	Eq.(18)
Attrition mills	ATTRITION	Limited by power consumption		Max. 224 kW

Table 4.3. Specifications and/or requirements of the inlet and product dimension

Biowaste (see Table 2.3)	Estimated inlet size	Pre-reduction equipments		Final reduction equipments	
		Roller crushers	Rotary cutters	Hammer mills	Attrition units
Wood wastes	75 mm	50 mm	-	4 mm	-
Grass and organic	100 mm	-	25 mm	-	4 mm
Agricultural wastes	100 mm	-	25 mm	-	4 mm
Manure and sludge	10 mm	-	-	4 mm	-
MSW	200 mm	50 mm	-	-	4 mm

4.2.6. Densification

Densification practices such as pelletization, briquetting or torrefaction are regarded as potential improvements for the production chains, although they have not been included in the analysis presented here. Torrefaction, in particular, seems to be a beneficial alternative to improve the reliability and uniformity of the feedstock as well as enhance gasification efficiency as torrefied wastes have a higher energy content compared to non-torrefied wastes [72, 73]. However, this efficiency is offset by the heat requirements for the torrefaction process. Torrefaction is a thermal treatment run at temperatures around 200-300^{o}C, at atmospheric pressure and in absence of oxygen. This pre-treatment technology upgrades the biomass properties to become more coal-like. Another major advantage is that the logistics costs can be reduced (as less water is transported) and the biowastes gain an hydrophobic nature, which means that they do not longer absorb water, and therefore, they can be stored outdoors without a need of shelters or warehousing.

4.2.7. Feeding Systems

Different systems have been developed for feeding biomass into a gasifier, i.e., screw feeders, rotary valve feeders, lock-hoppers and screw-piston feeders. A key parameter that influences the choice of a particular system is the gasification pressure against which the feeder has to operate. For instance, reactors operating at pressures up to 25 bar can be coupled to rotary valve feeders, lock-hoppers and screw-piston feeders are preferred for pressures up to 150 bar [51]. Screw feeders can only be applied for moderate pressures due to inherent gas leakage [51]. Hence, in our case, screw feeders are selected for atmospheric gasifiers and screw-piston feeders for pressurized gasifiers.

4.3. Cleaning Stages

Cleaning stages are required to avoid deactivation of the catalysts used in downstream reactors as well as to minimize SO_x and NO_x formation when burning remaining unconverted gases. Several compounds have been identified as potential poisons and their corresponding maximum allowed concentration is tabulated in the Table 4.4.

Cleaning stages in all production chains begins with particulates removal after gasification by using a multicyclone. Cyclones can remove particles down to 5μm. Syngas is then cooled to 55^{o}C prior to entering the subsequent stages, i.e., sulfur and ammonia removal. Sulfur (H_2S) is captured by means of absorption with an aqueous MDEA (N-methyl-diethanolamine) solution.

Table 4.4. Specifications for inlet streams prior to some catalytic reactors

Sections:	WGS Reactor [13, 76]	Methanation reactors [20]	Methanol reactor [13]	Fischer-Tropsch reactor [18, 77]	Reformer [13, 76]
Catalyst		Ni-based	$Cu/ZnO/Al_2O_3$	Fe/Co	Ni-based
Poisons:					
Ash / dust		<10 mg/Nm^3	< 0 ppm	0 ppb	
Tars		<5 mg/Nm^3	< dew point	0 mg/Nm^3	
S (H_2S + COS)	<0.01 ppm	<0.1 ppm	< 1 ppmV	<10 ppb	<0.25 ppm
N (HCN – NH_3)		<1 ppm	< 1 ppmV	<20 ppb	
Alkalines			< 10 ppb	<10 ppb	
Halogens (HCl + HF)		< 25 ppb	< 10 ppb	<10 ppb	< 1ppm
Heavy metals		<300 mg/Nm^3		unknown	
Others	Ar < 1ppm	Hg <0.05			

Amines have been used for acid gas removal (such as H_2S and CO_2) in industry for over 50 years, being MDEA the most widely used amine in existing installations [78, 79]. MDEA is here selected due to its low energy requirement for regeneration and higher selectivity over H_2S compared to CO_2. In fact, at this stage of cleaning, CO_2 removal is not desired as this gas is a reactant for some downstream catalytic reactors. MDEA solvent is also reported to be less corrosive. The principle of this cleaning process with MDEA is shown in Figure 4.4. In the first column (scrubber or absorber) sulfur (H_2S) is captured by the aqueous MDEA solution,

whose amine concentration is 40%. H_2S and a small fraction of CO_2 reacts with MDEA to form hydrogen sulfide and protonated amine (Eq. (25)), whereas CO_2 indirectly reacts with MDEA in the presence of water to form bicarbonate and protonated MDEA (Eq. (26)).

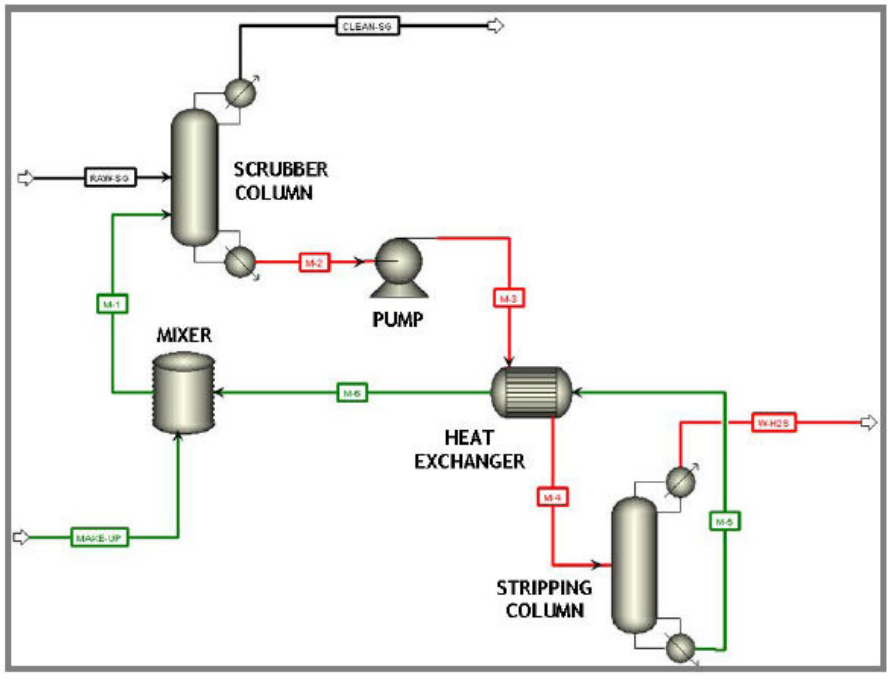


Figure 4.4. Simulation of acid gases removal (H_2S and CO_2) in Aspen Plus [56].

The chemical reactions taking place in the absorber are:

$$R_2R'N + H_3O^+ \Leftrightarrow R_2R'NH^+ + H_2O \quad (19)$$

$$CO_2 + 2H_2O \Leftrightarrow H_3O^+ + HCO_3^- \quad (20)$$

$$HCO_3^- + H_2O \Leftrightarrow H_3O^+ + CO_3^{2-} \quad (21)$$

$$2H_2O \Leftrightarrow H_3O^+ + OH^- \quad (22)$$

$$H_2S + H_2O \Leftrightarrow HS^- + H_3O^+ \quad (23)$$

$$HS^- + H_2O \Leftrightarrow S^{2-} + H_3O^+ \quad (24)$$

$$R_2R'N + H_2S \Leftrightarrow HS^- + R_2R'NH^+ \quad (25) = (19) + (23)$$

$$R_2R'N + CO_2 + H_2O \Leftrightarrow HCO_3^- + R_2R'NH^+ \quad (26) = (19) + (20)$$

The mechanism of the reaction (25) involves a proton transfer and, hence, this reaction is considered instantaneous with infinite reaction rate. The electrolyte package KEMDEA in Aspen Plus is being applied for the kinetics of the reactions whereas an absorber column (RADFRAC) working at 55°C and 1 bar has been used to model the absorber. The sulfur-charged solvent leaving the bottoms of the absorbed is then send to the regeneration column

(stripper) which works at higher temperature and pressure, i.e., 110°C and 2 bar. The stripper has also been modeled as a RADFRAC column with a condenser and reboiler. Acid gases (H_2S and CO_2) are released at the top of the column in the same chemical form in which they were absorbed. The regenerated solvent leaves the bottom of the column and it is also used to preheat the inlet stream of the stripping column. A make-up solution (10 wt% of MDEA) is also fed into the system in order to offset the MDEA losses occurring in the stripping column.

Clean syngas leaves the absorber column at around 40°C and it is then send to the ammonia removal unit, where gases are washed with an aqueous H_2SO_4 solution. HCl or other halogens) can be removed by adding Na or Ca based powdered absorbents. These are injected in the gas streams and removed in the dedusting stage. However, this has not been modeled in Aspen Plus. In some cases, H_2O and CO_2 are also needed to be removed in order to fulfill the specifications (see Table 4.4). CO_2 is removed by means of an absorption-stripping system similar to the aforementioned for H_2S capture. This process is especially suitable when CO_2 partial pressures are low, around 0.1 bar. On the other hand, H_2O is separated from raw SNG by passing it through a cooling closed cycle of ammonia and a phase separation unit, as shown in Figure 4.5.

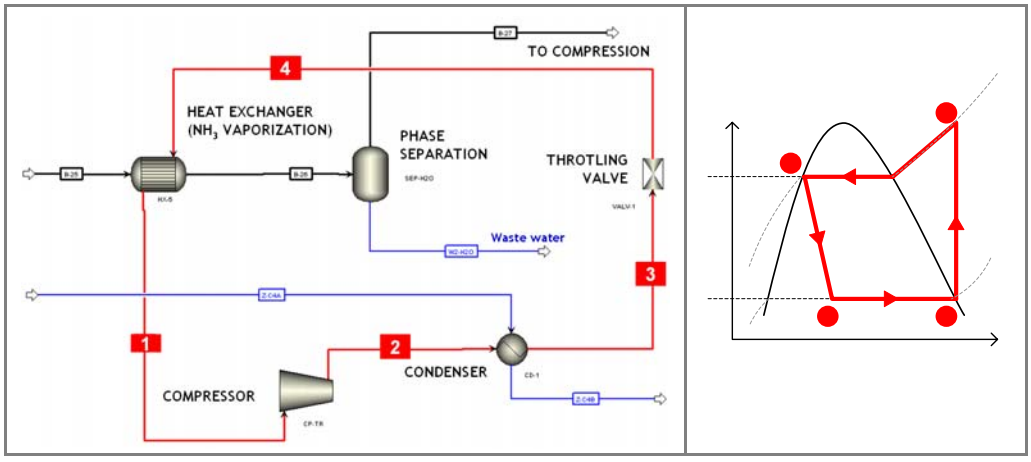


Figure 4.5. Simulation of H_2O removal by means of a closed cooling cycle with ammonia in Aspen Plus [56], and its corresponding T-s diagram.

Raw SNG entering the heat exchanger is cooled down to 10°C by a counter-current liquid ammonia solution at 0.1°C and 4.295 bar. Water is removed from the raw SNG and subsequently, dry gases are sent to the compression unit. Ammonia is then compressed and cooled to 20°C and 8.57 bar. After passing through a throttling valve, ammonia returns to its initial state of 0.1°C and 4.295 bar.

For the final application of biofuels in end-use devices, there are also limitations about the concentration of toxic compounds. Table 4.5 summarizes the main specifications for 4 common devices, i.e., a boiler, a gas engine, a gas turbine and a fuel cell. As observed, this specifications are less restrictive than the corresponding requirements of the catalytic reactors of the production chains (see Table 4.4). Hence, any additional cleaning unit is incorporated in the design of our processes.

Table 4.5. Specifications for inlet streams before entering a boiler, gas engine, gas turbine and fuel cell. More specific information about fuel cells is also given in Table 5.1

Poisons	Boiler [80]	Gas engine [80]	Gas turbine [81]	Fuel cell [80, 82]
Ash / dust	<1000 mg/Nm^3	50 mg/Nm^3	<2ppm	<0.1 mg/Nm^3
Tars	Dew point < 400^{o}C	Dew point < 10^{o}C	unknown	unknown
S (H_2S + COS)	<72 mg/Nm^3	<80 mg/Nm^3	<20 ppm	<1 mg/Nm^3
N (HCN + NH_3)	-	<50 mg/Nm^3	-	NH_3 can be a fuel
Alkalis	-	-	<0.03 ppm	-
Halogens (HCl + HF)	<35 mg/Nm^3	<100 mg/Nm^3	<1 ppm	<1 mg/Nm^3
Heavy metals	-	-	<0.05 ppm	-

(a) Specifications for Siemens Model VX4-3A gas turbine.

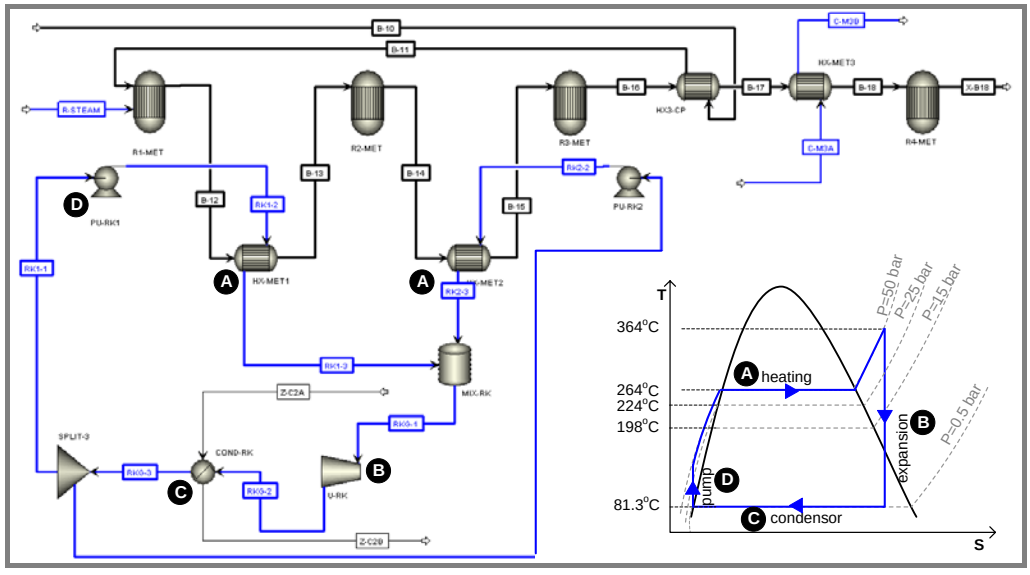


Figure 4.6. Simulation in Aspen Plus of the heat recovery during methanation (SNG production chain).

4.4. Heat Recovery

As pointed in Figures 4.7, 4.9-4.13, heat is supplied or needed at several points in the biofuel production process. For a better overall process efficiency, heat supply and demand are carefully matched so that more high quality heat is left to produce superheated steam, which is subsequently used for electricity production (Rankine cycles), in steam gasification, in WGS reactors or for biowastes drying. A considerable amount of heat is recovered after

gasification as the syngas needs to be cooled prior cleaning and compression. Another source of heat is due to cooling of methanation and Fischer-Tropsch reactors. Figure 4.6 shows the heat recovery taking place in the methanation section of the SNG production chain. In this case, several heat exchangers are placed among the 4 synthesis reactors (R1-MET to R4-MET) in order to control the temperature of inlet streams. Recovered heat is used to raise superheated steam at 364^{o}C and 50 bar. The corresponding thermodynamic T-s (temperature-entropy) diagram for the steam-water is also shown.

4.5. Synthetic Natural Gas (SNG)

Figure 4.7 schematically shows the main stages of the SNG production route. As observed, the main steps are pre-treatment, gasification, conditioning prior to the methanation unit and final upgrading to fulfill the strict specifications for natural gas pipelines, in particular composition, Wobbe-index, calorific value, and relative density.

For our scenario, low calorific natural gas distributed from Groningen fields is used as a reference (see Table 4.6). Low calorific natural gas contains more CO_2 and less CH_4 than high calorific natural gas. The hydrogen content should not exceed 10 mol%. At this hydrogen concentration, the produced SNG can be transported through the existing natural gas distribution infrastructure without any adjustment [83].

The index referred to as Wobbe number is indicative of the combustion energy being delivered to a burner at a constant pressure drop within a burner. The Wobbe index is defined as the ratio of the gross calorific value to the square food of the relative density of a gas. It can be calculated from the gas composition according to:

$$W_{in} = \frac{HHV}{\sqrt{\rho_g / \rho_{air}}} \tag{27}$$

where HHV is the gross calorific value (MJ/Nm^3), ρ_g is the density of the gas (kg/m^3) and ρ_{air} is the density of air (kg/m^3).

An atmospheric steam-blown gasifier is selected for the SNG chain. The Battelle indirect gasifier developed by FERCO corporation is here taken as a reference [53], and it consists of 2 physically separate units. The first unit is an atmospheric fluidized bed gasifier in which the biomass is converted into gases and residual char at a temperature of 700ºC. Residual char is burned in a second unit that provides sufficient heat for the gasifier. Heat transfer between reactors is accomplished by circulating sand between the gasifier and the combustor. The amount of residual char is regulated by adding more or less steam into the gasifier. Solid and gases are separated by using 2 cyclones, located at the exit of the gasifier and combustor respectively. The gasifier and the burner are both simulated in Aspen Plus as Gibbs reactors (RGIBBS). Moreover, many authors have used this type of reactor and their simulations show a good agreement with experimental results [58, 64, 70, 86].

Table 4.6. Comparison of Groningen natural gas with average natural gas from US pipelines. Adapted from [20, 84, 85]

Parameter	Groningen (the Netherlands)	US
Gross calorific value	31.6 – 38.7 MJ/Nm^3	35.4 MJ/Nm^3
Wobbe index (*)	43.4 – 44.4 MJ/Nm^3	-
Maximum liquid hydrocarbons	5 mg/Nm^3 below -3^{o}C at any P	-
Aromatic hydrocarbons	0.0025 – 0.1 mol %	-
Hydrocarbon dew point	-	264.9K at 5.5 MPa
Water dew point	- 8 ^{o}C at 70 bar	-
Total sulphur content	< 20 mg/Nm^3	23 – 114 mg/Nm^3
H_2S + COS	< 5 mg/Nm^3	< 5.7 mg/Nm^3 (H_2S)
NH_3	< 1 ppm	-
HCl	< 1 ppm	-
Mercaptans	< 6 mg/Nm^3	4.6 mg/Nm^3
H_2O	Dew point <-10^{o}C	64 - 112 mg/Nm^3
CH_4	~ 81 mol %	-
CO_2	< 3 mol %	1 – 3 mol %
O_2	< 0.0005 mol %	0 – 0.4 mol %
Hg	< 0.015 mg/Nm^3	-

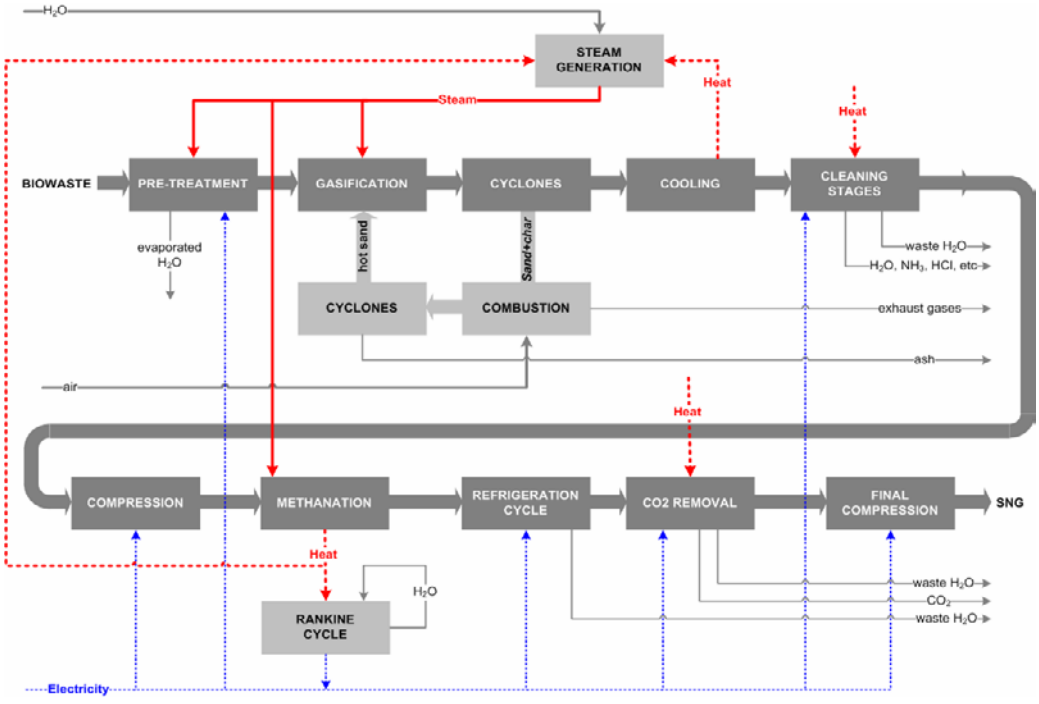


Figure 4.7. Schematic block diagram for the SNG production. Main inlet and outlet streams are indicated.

After gasification, cooling and cleaning stages, outlet gases are compressed to 28 bar and then fed to the methanation section. In this process CO and CO_2 react with H_2 to produce CH_4 according to the reactions:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H_{298K} = -206\ kJ/mol \tag{28}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H_{298K} = -165\ kJ/mol \tag{29}$$

As observed from the heat of reactions, this process is highly exothermic and, hence, part of the energy of the reactants is lost in the form of heat. Moreover, it cannot be conducted in a single catalytic reactor as it would result in thermal deactivation of the catalysts as well as lower conversion of the reactants. Consequently, a series of adiabatic reactors with intermediate heat exchangers are placed to control the temperature and achieve higher conversion. The number of catalytic reactors is fixed to achieve the maximum conversion of the reactants to methane. In our case, 4 adiabatic reactors are selected. Adding an extra reactor barely increases the amount of methane obtained as the reactants are almost fully converted, and the corresponding additional investments and operation costs are by far not offset. Temperatures of inlet gases are set to 398°C, 325°C, 300°C and 300°C respectively, as occurs in the ICI process [76]. Methanation reactors have been simulated as simple RGIBBS reactors that determine phase equilibrium by minimization of the Gibbs free energy.

For a common nickel-based catalyst, the operating range is between 260°C and 450°C. In order to overcome this limitation, ICI has developed a new high-nickel based catalyst (where nickel oxide is ~ 60%). This new catalyst seems to have the required activity, stability, and physical strength to methanate raw gases at a temperature of 750°C [76]. This ICI catalyst is selected for our simulation as it also has a water-shift activity required to adjust the H_2:CO ratio to the desired value of 3. However, apart from the aforementioned Eqs.((28)-(29)), inlet conditions of the methanation reactors are such that carbon could be formed via the reverse of reactions (9)-(10). The formation of carbon is undesired, because it results in loss of conversion efficiency, but also in deactivation of the catalyst by carbon deposition. Hence, steam is added into the first catalytic reactor to avoid carbon formation. After methanation, the outlet gases enter an ammonia cooling cycle to remove most of the water. Subsequently, CO_2 is separated from CH_4 by using a MDEA scrubbing system, working at the same conditions as the H_2S removal system. Heat removal after gasification and methanation is partly done to produce steam for the plant. Remaining heat is then employed to generate electricity in several steam turbines working in a Rankine cycle. Superheated steam is generated at 50 bar and 364°C, and expanded to 0.5 bar and 81.3°C.

Five biowastes streams (see Table 2.3) have been converted to SNG via the aforementioned process. Process conditions of the upgrading stages (H_2O and CO_2 removal) have been adjusted to fulfill the Groningen gas specifications (see Table 4.6), in particular the Wobbe index, considered as the functional parameter and whose target value has been set to 43.5 MJ/Nm^3. Under this constraint, the other requirements are also fulfilled, i.e., gross calorific value and concentration of main compounds and toxicity. Comparison of efficiencies is based on the same SNG output (i.e., 11,845 kg/hr) with the same quality or Wobbe index (i.e., 43.5 MJ/Nm^3). Table 4.7 compares the efficiency of the biowaste-to-SNG conversion in terms of exergetic efficiency and mass conversion. More details about calculation of these efficiencies are given in section 6. Table 4.8 summarizes the properties and composition of the SNG produced from the five different biowastes. As observed, the SNG obtained have similar quality except for stream D (manure and sludge), whose Wobbe index is below the range specified for the Groningen gas. In this case, separation membranes should be

incorporated into the process in order to remove part of the nitrogen, which negatively affects the Wobbe index.

Table 4.7. Comparison of efficiencies for the different biowaste-to-SNG options

Biowaste ➡ Parameter ⬇	wood and forest (A)	grass and organic (B)	agricultural wastes (C)	manure and sludge (D)	MSW (E)
Mass conversion yield μ (kg SNG/kg biowaste)	26%	13%	20%	11%	17%
Energy efficiency Ψ_{HHV} (HHV products/HHV biowaste)	72%	70%	71%	65%	69%
Exergetic efficiency Ψ (exergy products/exergy inputs)	69%	68%	71%	66%	67%

Table 4.8. Properties and composition of the SNG produced from different biowastes

Biowaste ➡ Parameter ⬇	wood and forest (A)	grass and organic (B)	agricultural wastes (C)	manure and sludge (D)	MSW (E)
Gross calorific value (MJ/Nm^3)	33.4	33.1	33.0	32.3	33.1
Wobbe (MJ/Nm^3)	43.5	43.5	43.5	42.3 [(a)]	43.5
H_2O	1%	1%	1%	1%	1%
N_2	3%	4%	3%	9% [(a)]	2%
O_2	0%	0%	0%	0%	0%
H_2	12%	13%	13%	11%	13%
CO_2	3%	2%	3%	0%	3%
CH_4	80%	79%	79%	78%	79%
traces others compounds	1%	1%	1%	1%	2%
Total sulphur content (mg/Nm^3)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Solid hydrocarbons	none	none	none	none	none
Aromatic hydrocarbons	none	none	none	none	none
Mercaptans	none	none	none	none	none
Hg (mg/Nm^3)	none	none	none	none	none

[(a)] Wobbe index of 43.5 MJ/Nm3 is not achieved.

The biowastes here studied have different ultimate and proximate analysis (see Table 2.3) values which directly affect the amount of SNG that can be produced. SNG basically contains methane (~80%), which is formed by carbon and hydrogen atoms. Therefore, it is expected that feedstock containing more carbon and hydrogen would lead to a higher production of methane or SNG. That is clearly the case of the wood used in our simulations (i.e., stream A in Table 2.3). Agricultural and municipal wastes (stream C and E) have less carbon and hydrogen than wood, and as expected, more feedstock (i.e., kg/hr on wet basis) is needed in

order to produce the same amount of SNG. The worst cases are the wet streams D and B (manure and grass), which have a relatively low carbon and hydrogen content. These observations are shown in Figure 4.8.

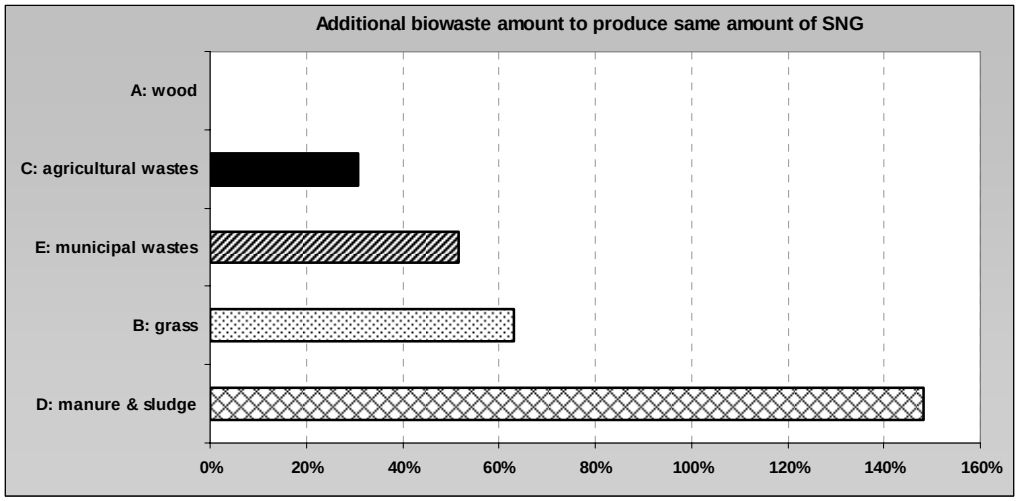


Figure 4.8. Additional biowaste amount needed to produce the same amount of SNG (i.e., 11,845 kg/hr) with the same quality (i.e., Wobbe index equal to 43.5 MJ/Nm^3). Values are on a wet basis (kg/hr), i.e., in the state of the received feedstock. For instance, 1 kg of wood would produce the same amount of SNG (i.e., 0.26 kg) as 1.48 kg of manure.

The inherent implications of using more mass of feedstock are various. Firstly, the logistics costs are higher as more biowaste has to be collected and transported. Secondly, processing equipment, in particular, pre-treatment units such as drying, are larger, which directly increase the investment costs. Moreover, more energy, utilities and human labor are required, which directly increase the operational costs. However, in some cases, wastes with "worst" quality are cheaper, which could ultimately compensate the required operational and labor costs to process these streams.

4.6. Methanol

The production of methanol from synthesis gas was first developed at BASF Germany in 1922. This process used a zinc oxide-chromium oxide catalyst with poor selectivity and it also required very extreme conditions with pressures exceeding 300 bar. More selective catalysts discovered in the 1970's, allowed to build larger plants with higher energy and cost efficiency. Current research focus on shifting the equilibrium to achieve higher conversion per pass. Figure 4.9 schematically shows the main stages for the production of methanol. As for the case of SNG, the main steps are pre-treatment, gasification, conditioning prior to the methanol reactor unit and final upgrading to reach a methanol purity above 98.6 mol % (dry basis).

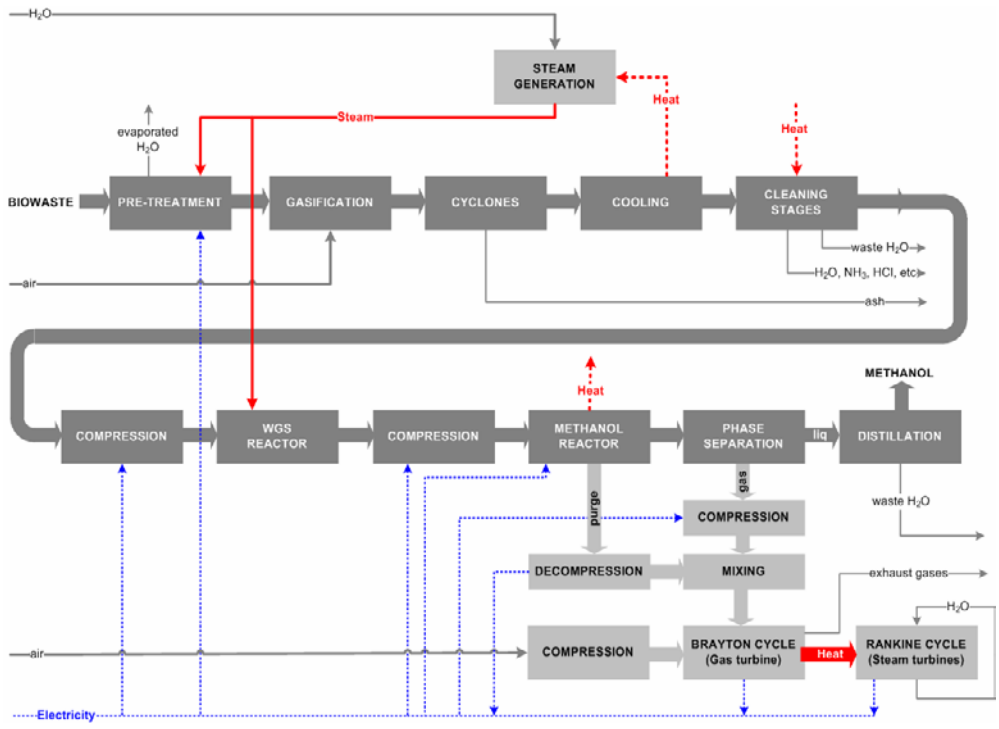


Figure 4.9. Schematic block diagram for the methanol production. Main inlet and outlet streams are indicated.

Part of the unconverted reactants and purge from the methanol reactor is used to produce electricity in a combined Rankine-Brayton cycle. An atmospheric air-blown gasifier is used in this process, working at 1000°C and 1 bar. In this case, air or oxygen is preferred as oxidizing agent instead of steam in order to get a higher content of the "building agents" CO and H_2 and minimize hydrocarbons formation, such as CH_4 or C_2H_6. After gasification, outlet gases are also cooled down before entering the required cleaning stages. Heat removal is here entirely used for producing pressurized steam. Clean gases are compressed to 25 bar and send to a WGS reactor where the H_2:CO ratio is adjusted to 2.

The WGS reactor is simulated as a phase equilibrium reactor (REQUIL) from the Aspen Plus library, whose main feature is that it calculates equilibrium by solving stoichiometric chemical and phase equilibrium equations. The reaction taking place is the WGS reaction (Eq.(5)). Due to the high catalyst selectivity all gases, except those involved in the WGS reaction, are inert. The reaction is exothermic, independent of pressure and proceeds nearly to completion at low temperatures.

In the case of methanol synthesis, the gas is only partially shifted to a suitable H_2:CO ratio of 2. Subsequently, the outlet stream is further compressed and fed to a catalytic methanol reactor, operated at 77 bar and 200°C. This methanol reactor has been simulated as a stoichiometric reactor (RSTOIC), and the ICI low pressure methanol process is taken as a reference [76, 87, 88]. Table 4.9 presents the possible operation range of the ICI process together with examples of other commercial processes.

Table 4.9. Heterogeneous catalytic processes for methanol synthesis [88]

Process	Catalyst	Temperature (^oC)	Pressure (bar)
Nissui-Topsoe	$CuO\text{-}ZnO\text{-}Cr_2O_3$	230 – 260	100 – 150
BASF	$CuO\text{-}ZnO\text{-}Al_2O_3$	200 – 350	50 – 250
ICI	$CuO\text{-}ZnO\text{-}Al_2O_3$	220 – 280	50 – 100
Lurgi	CuO-ZnO	230 – 250	40 – 50
Mitsubishi Gas Chemical	$CuO\text{-}ZnO\text{-}Al_2O_3$	250 – 275	50 – 120

In order to establish an uniform temperature in the ICI reactor, gases are fed at various locations along the length of a catalytic bed. Methanol is here produced by hydrogenation of carbon oxides over a Cu/Zn/Al catalyst ($CuO\text{-}ZnO\text{-}Al_2O_3$), according to the following reactions:

$$CO + 2H_2 \Leftrightarrow CH_3OH \qquad \Delta H^o_{298K} = -90.6\ kJ/mol \qquad \kappa = 15\% \quad (30)$$

$$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O \qquad \Delta H^o_{298K} = -49.5\ kJ/mol \qquad \kappa = 3\% \quad (31)$$

where κ is the conversion degree [89]. As conversion cannot be accomplished in one pass, the unreacted syngas is recycled back to the methanol reactor in order to increase the conversion efficiency. Recycling is done via a system consisting of a condenser, a purge valve and a recycle compressor. The condenser works at 45^{o}C and it is used to separate the unreacted syngas from the liquid methanol. About 90% of the unreacted syngas is recompressed to 77 bar and recycle back to the reactor. Compression is required due to the volume decrease occurring in the reactor (Eq.(30)-(31)). Remaining 10% is purged and send to a pressurized combustor where it is burned to provide heat for a combined Brayton and Rankine cycle. Electricity and heat are produced herein. The Brayton cycle consist of a combustor working at 15 bar, a gas turbine and a series of heat exchangers that provide heat for the Rankine cycle. Superheated steam is generated at 50 bar and 364^{o}C, and expanded to 0.5 bar and 81.3^{o}C by means of 2 turbines with intermediate superheating. Liquid methanol leaving the condenser of the reactor system is sent to an atmospheric distillation column where it is separated from water and other minor impurities. The distillation column is simulated as a RADFRAC unit that performs rigorous calculations.

Unlike ethanol production that consumes clean food crops or lignocellulosic materials, methanol plants can use any organic source, including wood, wood wastes, grass, agricultural crops and their by-products, animal wastes (e.g., manure), sludge and municipal waste. The biowastes streams from Table 2.3 are again simulated in Aspen Plus, giving the results summarized in Table 4.10.

4.7. Fischer-Tropsch

The conversion of the synthesis gas to aliphatic hydrocarbons over metal catalysts was first discovered by Franz Fischer and Hans Tropsch at the Kaiser Wilhelm Institute in 1923. They discovered that CO hydrogenation over iron, cobalt or nickel catalysts at 180-250°C and

atmospheric pressure yields a product mixture of linear hydrocarbons and some oxygenates. However, Fischer-Tropsch synthesis was not applied at commercial scale until 1930's, when Germany started producing Fischer-Tropsch liquids from coal to power vehicles. Nowadays, the technology is well proven for feedstock such as coal and natural gas, being Sasol in South Africa and Shell in Malaysia the leading plants worldwide. Conversely, Fischer-Tropsch synthesis from biomass derived syngas has not been scaled up to commercial plants yet, although Choren industries [90] are planning to commission a plant with a capacity of 200,000 ton/yr by 2010. The process for converting biomass into Fischer-Tropsch liquids is similar in many aspects to that for coal conversion.

Table 4.10. Comparison of efficiencies and biofuel quality for the different biowaste-to-methanol options

Biowaste ➡ Parameter ⬇	wood and forest (A)	grass and organic (B)	agricultural wastes (C)	manure and sludge (D)	MSW (E)
Mass conversion yield μ (kg SNG/kg biowaste)	48%	27%	33%	16%	32%
Energy efficiency Ψ_{HHV} (HHV products/HHV biowaste)	69%	64%	64%	61%	64%
Exergetic efficiency Ψ (exergy products/exergy inputs)	58%	57%	59%	56%	58%
Biofuel quality (methanol purity)	98.8 mol% 98.4 wt%	98.9 mol% 98.5 wt%	98.8 mol% 98.4 wt%	99.1 mol% 98.7 wt%	98.9 mol% 98.5 wt%

Figure 4.10 shows the block diagram of our process simulation in Aspen Plus. An atmospheric air-blown gasifier working at 900°C is used in this chain. Outlet gases are again cooled down to 55°C and send to the corresponding cleaning stages.

In this case, heat removal is entirely used in a Rankine cycle to produce electricity. The cycle is working at the same conditions as in the SNG chain, where steam is expanded from 50 bar and 364°C to 0.5 bar and 81.3°C. Clean gases are then compressed to 25 bar and send to a WGS reactor to adjust the H_2:CO ratio at 2.13.

Subsequently, syngas is converted to a mixture of different hydrocarbons in a catalytic Fischer-Tropsch reactor operated at 260°C and 23 bar. The reactor is simulated as a RGIBBS and the total single-pass conversion of H_2 and CO is assumed to reach 80% [91]. Heat removed from the process is used to produce steam required for the WGS reactor and the drying stage. The Fischer-Tropsch synthesis can be described by the set of equations presented in Table 4.11, where the main reactions taking place are hydrocarbons chain formation (Eq.(32)-(33)).

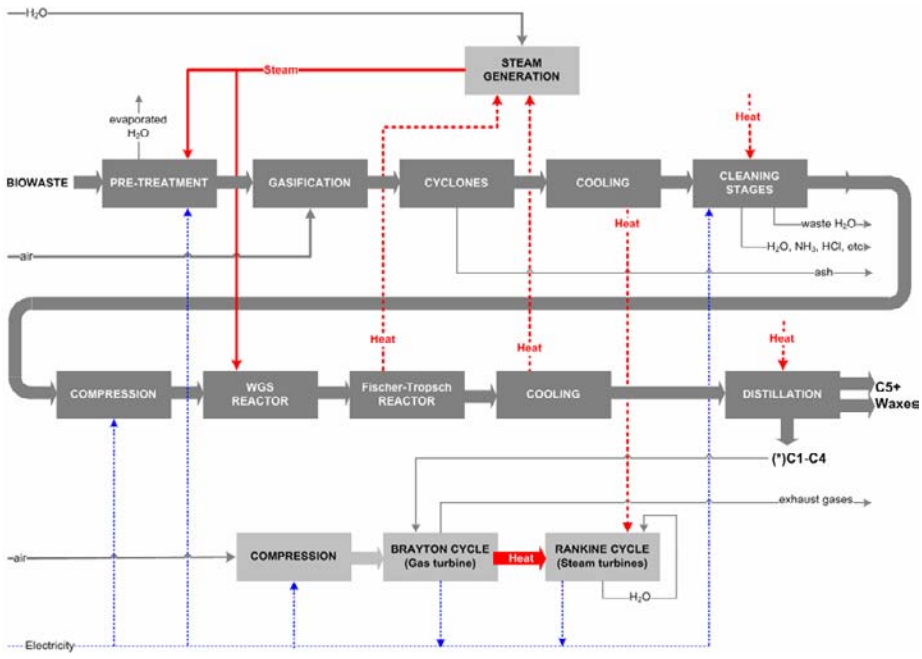


Figure 4.10. Schematic block diagram for the Fischer-Tropsch fuels production. Main inlet and outlet streams are indicated.

Table 4.11. The main Fischer-Tropsch chemical reactions

Reaction	Equations	ΔH_{298} (kJ/mol)	Eq.
Main reactions:			
Paraffins (alkanes)	$nCO + (2n+1)H_2 \leftrightarrow C_nH_{2n+2} + nH_2O$		(32)
Methanation (n=1)	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	- 206	(8) = =(5) + (7)
Olefins	$nCO + 2nH_2 \leftrightarrow (-CH_2-)_n + nH_2O$	+159	(33)
Water-gas-shift (WGS)	$CO + H_2O \leftrightarrow CO_2 + H_2$	- 41	(5)
Side reactions:			
Alcohols	$nCO + 2nH_2 \leftrightarrow C_nH_{2n+2}O + (n-1)H_2O$		(34)
Boudouard	$C + CO_2 \leftrightarrow 2CO$	+ 172	(10)

The most common catalysts for Fischer-Tropsch synthesis are metals of group VIII. Among them, Fe-, Co-, Ni- and Ru- catalysts are considered to have sufficient activity for industrial applications. Table 4.12 summarizes the main characteristics, operation conditions and price relation of these catalysts. The Ru- and Rh- catalyst are the most active but they are also very expensive due to their limited availability and, hence, they are not suitable for large-scale installations. The Ni- catalyst is also notably active but it produces a higher amount of

methane and it also forms volatile and very poisonous carbonyls which, in turn, results in metal loss.

Table 4.12. Comparison of main catalysts for Fischer-Tropsch synthesis. Relative prices in 2007

Metal (catalyst)	Price ratio [94]	Advantages	Disadvantages
Iron	1	Low costs High selectivity to olefins Higher WGS promotion	Lower activity than Co Lower lifetime than Co Lower heavy CxHy selectivity (=low diesel output)
Cobalt	235	High activity Longer lifetime than Fe Higher heavy CxHy selectivity	Higher costs than Fe Lower WGS promotion
Nickel	140	High activity	Higher selectivity to methane Forms volatile carbonyls (=loss of metal)
Ruthenium	76000	Higher activity than Fe,Co,Ni	Higher costs than Fe,Co,Ni
Rhodium	824000	The most active catalyst	Excessive costs (=none commercial application)

Therefore, nowadays, Fe- and Co- are the two only practical alternatives for large scale installations. Co- catalyst is selected for our simulation due to its high selectivity towards to linear alkanes, longer life-time and higher activity [92, 93]. However, since Co-catalyst has a limited WGS activity, a specific WGS reactor is placed prior to the Fischer-Tropsch catalytic reactor in order to adjust the H_2:CO ratio.

Formation of hydrocarbons is assumed to follow the ideal Anderson-Schulz-Flory equation, characterized by the chain growth probability factor α, whose mathematical representation is given by Eq. (35):

$$\log \frac{W_n}{n} = n \cdot \log \alpha + \log \frac{(1-\alpha)^2}{\alpha} \tag{35}$$

where W_n is the mass fraction of a product consisting of n carbon atoms. The growth factor α is highly dependent on reaction conditions and the catalyst type. An increase of temperature is translated into a decrease of the α factor, and the same effect is observed when increasing H_2/CO ratio.

Some authors have reported typical ranges of a on Fe-, Co-, and Ru-, and their values are presented in Table 4.13.

In our simulation, the factor α is been calculated from Lox and Froment equation (see Eq.(36)), which is based on experiments using a precipitated iron catalyst [98]. This model was used by Prins et al. to simulate a Co-based catalytic reactions with the assumption that industrial catalysts will follow similar selectivities [91].

Table 4.13. Ranges values of chain growth probability factor α

Metal (catalyst)	Range values	Reference
Fe-	0.50 – 0.70 0.66 – 0.79	[95] [96]
Co-	0.70 – 0.80 0.73 – 0.95	[95] [96, 97]
Ru-	0.85 – 0.95	[95]

The model predicts that the rate determining processes are the adsorption of CO and desorption of hydrocarbon products.

$$\alpha = \frac{R_{propagation}}{R_{propagation} + R_{termination}} = \frac{k_{HC1} \cdot P_{CO}}{k_{HC1} \cdot P_{CO} + k_{HC5} \cdot P_{H_2} + k_{HC6}} \tag{36}$$

where R is the rate of either propagation and termination, k_{HC1} is the rate constant for adsorption of CO on an active site (equal to 1.22×10^{-5} mol/g.s.bar), k_{HC5} is the rate constant for desorption of paraffins by hydrogenation of active site (mol/g.s.bar), k_{HC6} is the rate constant for desorption of olefins from active site (mol/g.s), P_{CO} is the partial pressure of CO (bar) and P_{H2} is the partial pressure of H_2 (bar). The rate constants (k_{HC5} and k_{HC6}) follow the Arrenhius law and they are calculated by applying the following experimental relations:

$$k_{HC5} = A_i \times \exp(-E_i/RT) = 423.3 \times \exp(-94500/RT) \tag{37}$$

$$k_{HC6} = A_i \times \exp(-E_i/RT) = 2712508.9 \times \exp(-132300/RT) \tag{38}$$

where R is the universal gas constant and T is the temperature. Values of the α-factor for all biowastes are in the range of 0.942-0.946 (diluted gases with N_2) and 0.958-0.960 (undiluted gases). These values are similar to those reported results of Prins *et al*. [91]. After the Fischer-Tropsch reactor, the products are cooled to 50°C in order to separate the liquids hydrocarbons from the tail gas (C1-C4). Conventional refinery processes can be used for upgrading C_{5+} Fischer-Tropsch fuels but this section has not been included in our simulation. Moreover, tail gas containing light hydrocarbons (C1-C4) can be either reformed and recycled back to the Fischer-Tropsch reactor, or combusted to produce electricity in a combined cycle similar to the one used in the methanol chain (see section 4.6). Separation of the C3-C4 fraction from the tail gas can be also done by cooling or distillation but whether this is economically attractive is still questionable. Proposed improvements are shown in Figure 4.11. Results from Aspen Plus simulations are presented for each biowaste stream in Tables 4.14 and 4.15. As for the case of methanol and SNG production, dry streams (A) and (C) again achieve higher efficiencies. Unlike gasoline and diesel, the Fischer-Tropsch fuels obtained are totally free of sulfur and contain very few aromatics. This results in lower emission levels when Fischer-Tropsch fuels are used in internal combustion engines of vehicles. Another application could be in fuel cell vehicles (FCV's), which require a very clean fuel in order to prevent damage of the fuel cell catalyst. Potential application of Fischer-Tropsch fuels are discussed with more detail in section 5.

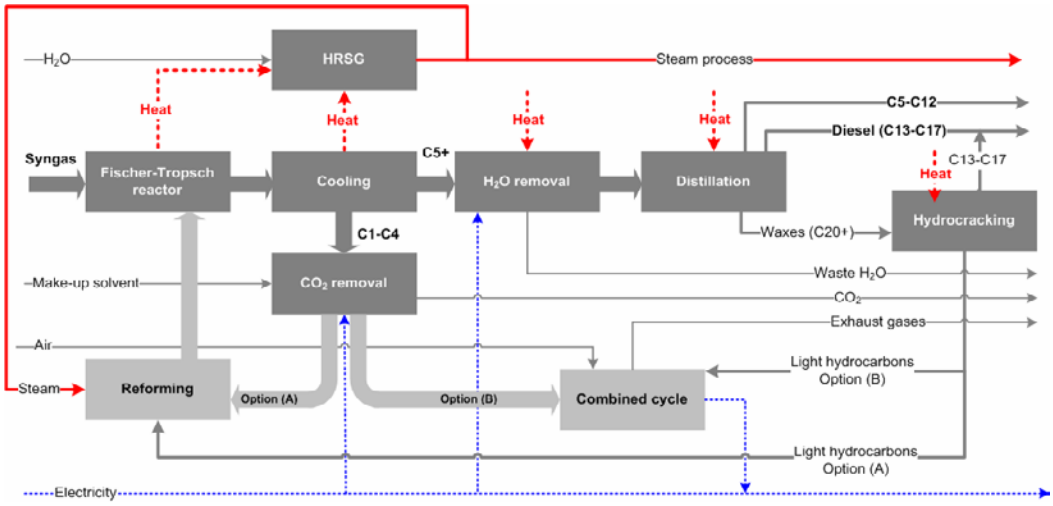


Figure 4.11. Potential improvements for upgrading Fischer-Tropsch fuels.

Table 4.14. Comparison of efficiencies and Fischer-Tropsch fuels quality for the different biowaste streams

Biowaste ➡ Parameter ⬇	wood and forest (A)	grass and organic (B)	agricultural wastes (C)	manure and sludge (D)	MSW (E)
Mass conversion yield μ (kg SNG/kg biowaste)	18%	12%	16%	8%	12%
Energy efficiency Ψ_{HHV} (HHV products/HHV biowaste)	67%	67%	69%	65%	64%
Exergetic efficiency Ψ (exergy products/exergy inputs)	58%	57%	62%	53%	55%

Table 4.15. Properties of Fischer-Tropsch fuels

Biowaste ➡		all streams	wood and forest (A)	grass and organic (B)	agro wastes (C)	manure and sludge (D)	MSW (E)
Parameters ➡ Components⬇		HHV (MJ/kg)	Mass fraction (CO_2, N_2 and H_2O free)				
Unconverted syngas	CO + H_2	24.7	35.5	35.5	35.1	35.5	35.4
Tail (fuel gas + LPG)	C1-C4	51.0	3.5	3.2	2.7	3.3	3.6
Gasoline	C5-C12	48.1	14.7	13.7	12.1	14.2	15.1
Naptha	C8-C12						

Table 4.15. (Continued)

Biowaste ➡		all streams	wood and forest (A)	grass and organic (B)	agro wastes (C)	manure and sludge (D)	MSW (E)
Kerosene (jet fuel)	C11-C13						
Diesel (fuel oil)	C13-C17	47.4	10.3	9.9	9.2	10.1	10.5
Middle distillates	C18-C20	47.2	5.9	5.8	5.5	5.8	5.9
Waxes	C20+	47.1	30.1	31.9	35.3	31.1	29.4

4.8. Hydrogen

Hydrogen can be produced from different sources, ranging from hydrocarbons, water or even biomass. Nowadays, the main processes for hydrogen production are steam-methane reforming (SMR) and/or catalytic decomposition of natural gas (48%), partial oxidation of heavy crude oils (30%), coal gasification (18%) and electrolysis of water (4%) [99]. Hence, about 96% of the hydrogen is produced from fossil fuels, liberating more than 300 Mton/year of CO_2. In other to overcome this major environmental problem, recent investigations are focus on developing more sustainable technologies. Hydrogen production from biomass gasification and further catalytic conversion is one of the potential options that is being analyzed in several projects such as the CHRISGAS (Värnamo, Sweden) [4] and AER GAS-II (Gussing, Austria) [100]. Figure 4.12 shows the block diagram of our hydrogen chain simulation in Aspen Plus, which is based on the aforementioned processes.

The gasification and downstream cleaning units are similar to those used for the SNG production. A Battelle-type steam-blown gasifier is selected as more hydrogen is obtained when steam is the gasifying medium (see Figure 4.6). After the cleaning stages, the syngas is compressed and send to a reformer unit that is driven by steam addition over a Ni-based catalyst and operated at 35 bar and 850^{o}C. In the reformer, methane, tars and light hydrocarbons are reconverted to CO and H_2. This process is similar to the catalytic steam reforming of natural gas, but in this case, the steam to carbon ratio is fixed to 3.5 as a small fraction of lighter hydrocarbons are also present. The reforming reactions are strongly endothermic, so the forward reaction are favored by high temperature and low pressure, although elevated pressures benefit economically [13, 14]. The governing reactions are described by the reverse of Eq.(8) and the following equations:

$$C_2H_4 + 2H_2O \leftrightarrow 2CO + 4H_2 \qquad \Delta H^o_{298} = +210\ kJ/mol \tag{39}$$

$$C_2H_6 + 2H_2O \leftrightarrow 2CO + 5H_2 \qquad \Delta H^o_{298} = +347\ kJ/mol \tag{40}$$

A significant portion of the WGS reaction also takes place (Eq.(5)) and it brings the reformer products to chemical equilibrium [101]. The reformer is modeled as a RGIBBS reactor, where the inlet stream is preheated with the hot stream leaving the unit so as to reduce the external heat supply.

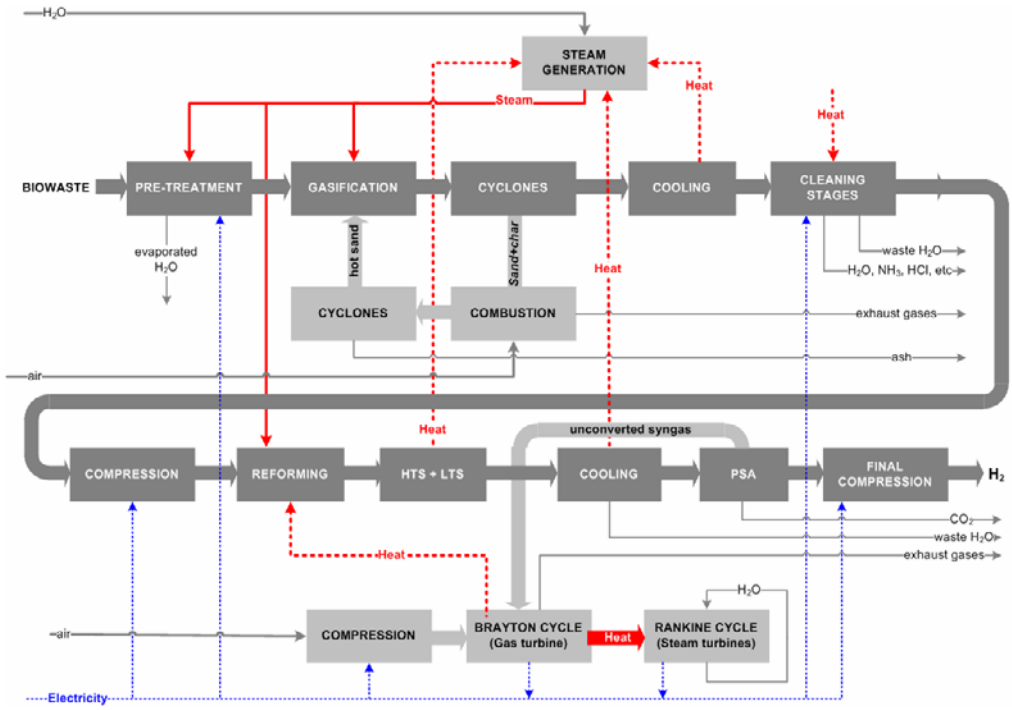


Figure 4.12. Schematic block diagram for the hydrogen production. Main inlet and outlet streams are indicated.

Remaining heat is supplied by the hot flue gas leaving the combustor of the combined cycle placed downstream. After reforming, hydrogen content of the syngas can still be increased by using a WGS process. Unlike the reforming reactions, the WGS shift reaction is moderately exothermic, favored by low temperatures and it is not affected by pressure [13, 76]. Moreover, due to the high catalyst selectivity, all gases except those involved in the WGS reaction act as inerts. However, under adiabatic conditions, complete conversion in a single bed catalyst is not possible due to thermodynamic limitations. Therefore, two subsequent high temperature (HTS) and low temperature (LTS) shift reactors with intercooling are placed to assure maximum conversion of CO [13, 76, 102]. Both reactors are simulated as stoichiometric RSTOIC reactors and the operational conditions for the first (HTS) and second (LTS) shift reactor are 435^{o}C and 30 bar, and 220^{o}C and 25 bar respectively, whereas the corresponding catalysts are Fe_3O_4-Cr_2O_3 (HTS) and ZnO-CuO (LTS). Copper catalysts are more prone than iron catalysts to deactivation by sulfur compounds [76]. Hence, the cleaning stages are designed to meet the requirements of the copper catalyst of the LTS.

Subsequently, the hydrogen-rich syngas is cooled down to remove most of the water and, finally, it is purified in a Pressure-Swing-Adsorption unit (PSA). This PSA process is based on the difference in adsorption behaviour between different molecules, i.e., it separates components of a gaseous stream by a selective adsorption over a solid at high pressure, and subsequent desorption unit containing zeolite molecular sieve operated at low pressure. Adsorption and desorption takes place in 2 separate beds, so that the process can be run continuously [13, 101, 102]. About 85% of the H_2 is recovered and a purity of 99% is achieved. However, this system has the limitation that the inlet stream must contain at least

70 mol% of H_2. Therefore, whenever the hydrogen concentration is lower, a recycle is incorporated to achieve the minimum level. Unconverted syngas is then sent to a pressurized combined Brayton-Rankine cycle to produce electricity and heat for the plant. Results from Aspen Plus simulations are presented for each biowaste stream in Table 4.16. As for the case of other chains, the driest streams (A) and (C) again achieve higher efficiencies.

Table 4.16. Comparison of efficiencies and biofuel quality for the different biowaste-to-hydrogen options

Biowaste ➡ Parameter ⬇	wood and forest (A)	grass and organic (B)	agricultural wastes (C)	manure and sludge (D)	MSW (E)
Mass conversion yield μ (kg SNG/kg biowaste)	9%	6%	7%	7%	6%
Energy efficiency Ψ_{HHV} (HHV products/HHV biowaste)	66%	66%	67%	66%	65%
Exergetic efficiency Ψ (exergy products/exergy inputs)	55%	54%	57%	55%	54%
Biofuel quality (hydrogen purity)	99%	99%	99%	99%	99%

In 2005, global hydrogen production already achieved $5x10^{11}$ Nm^3 per year (i.e., 44.5 Mton/yr), where the main consumption accounts for ammonia production (50%), petroleum refining (37%), methanol and other chemicals synthesis (13%) [60]. However, in this chapter, we propose the use of hydrogen as biofuel for transportation instead as it may become one of the key fuels for the future. In fact, the US Department of Energy (2003) estimates that by 2040 the world energy demand of hydrogen use in fuel cell powered cars and light trucks will be approximately 150 Mton/year [60]. Application of hydrogen is discussed in section 5.

4.9. Heat and Electricity

The last option analyzed for biomass conversion is to directly produce electricity and heat by means of a combined Brayton-Rankine cycle, as schematically shown in Figure 4.13. The concept is similar to the one applied in already existing IGCC (Integrated Gasification Combined Cycle) plants based on coal and, more recently, on biomass (BIGCC). The major benefit of this concept compared to traditional pulverized coal combustion plants is that they attain higher efficiencies, i.e., 40-50% (electrical) or 85-90% (overall) compared to 20-40% (electrical) or 80-88% (overall) for coal combustion [4]. A higher efficiency is also translated into a 20% reduction of CO_2 emissions per unit of electricity generated [103]. Moreover, since in the IGCC process purities are removed prior to combustion, the overall environmental impact is further reduced. However, the high cost of IGCC is the biggest obstacle to its wider integration into the power market.

The world's first BIGCC demonstration plant was the Värnamo plant in Sweden, which was mothballed after 6 years of operation in 1999, and later reconverted to synthesize other biofuels under the European project CHRISGAS [4]. The power and heat generation of this plant was $6MW_e$ and $9MW_{th}$ respectively, with an electric efficiency of 32% and a total net

efficiency of 83%. New generation BIGCC plants with better efficiencies are also under development in order to become more cost effective. In particular, emphasis is given to design modified gas turbines that can use gaseous fuels with lower calorific value. Figure 4.13 shows the block diagram of our electricity generation plant in Aspen Plus.

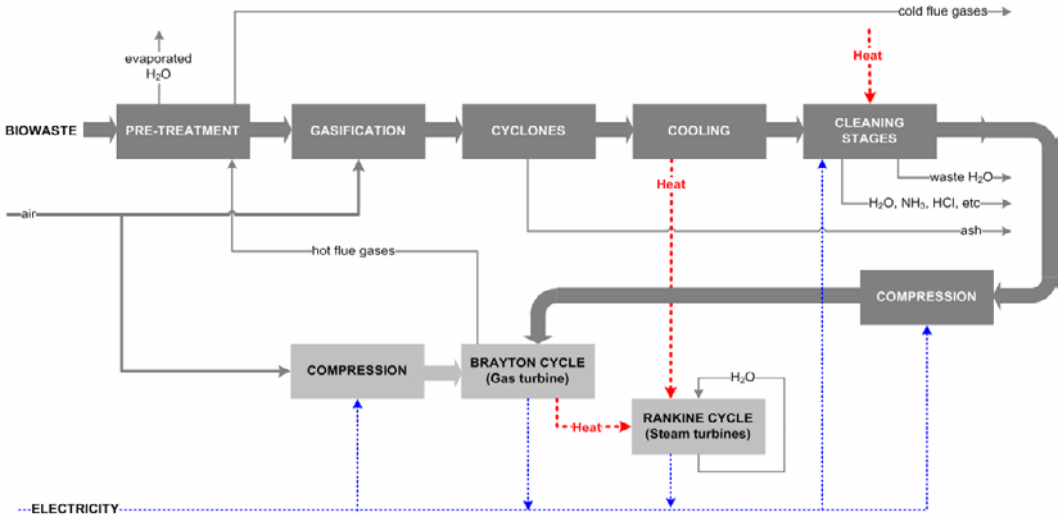


Figure 4.13. Schematic block diagram for electricity generation in a combined cycle. Main inlet and outlet streams are indicated.

Unlike the Värnamo plant, the gasifier is operated at atmospheric pressure and 900°C. As for all the previous processes, gases leaving the gasifier are cooled down to 55°C and send to the corresponding cleaning units in order to remove sulphur and nitrogen compounds, i.e., the precursors of acid rain and photochemical smog. The low temperature and oxygen deficient conditions of the gasifier do not favor NO_x and SO_x generation but the reduced forms NH_3 and H_2S are inevitably produced. In the case that the cleaning stages were not incorporated to the process, these two compounds would be further converted to SO_x and NO_x after combustion, contributing to 75-95% of the total NO_x released. The remaining amount of nitrogen compounds would originate from the injected air. Heat removal is also used here to operate a steam turbine working in a simple Rankine cycle, where expansion takes place from 50 bar and 364°C to 0.5 bar and 81.3°C. Clean gases are then fed to a combined cycle consisting of a Brayton and a second Rankine cycle.

A single gas turbine is used in the Brayton cycle where hot gases are expanded from 1200°C and 15 bar to 605°C and 1 bar. This mild-hot stream is still used to provide part of the heat required for the Rankine cycle. Another heat source for the Rankine cycle is taken from the cooling of the gases leaving the combustor that have a temperature higher than 1200°C, i.e., the limited temperature for commercial turbines [104]. Hence, the gases need to be cooled before entering the expansion turbine of the Brayton cycle. This second Rankine cycle operates with 2 turbines with inter-heating to 364°C. The first steam turbines operate from 50 bar to 25 bar whereas the outlet of the second stream is 0.5 bar and 81.3°C. Electricity can be then sent to the grid. Figure 4.14 shows the combined cycle simulation in Aspen Plus with the corresponding thermodynamic graph T-s (temperature-entropy). Results from Aspen Plus

simulations are presented for each biowaste stream in Table 4.17. As for the case of other chains, dry streams (A) and (C) achieve higher efficiencies.

Table 4.17. Comparison of efficiencies for different biowaste-to-electricity options

Biowaste ➡ Parameter ⬇	wood and forest (A)	grass and organic (B)	agricultural wastes (C)	manure and sludge (D)	MSW (E)
Energy efficiency Ψ_{HHV} (HHV products/power)	46%	46%	47%	43%	44%
Exergetic efficiency Ψ (exergy products/exergy inputs)	43%	42%	45%	42%	40%

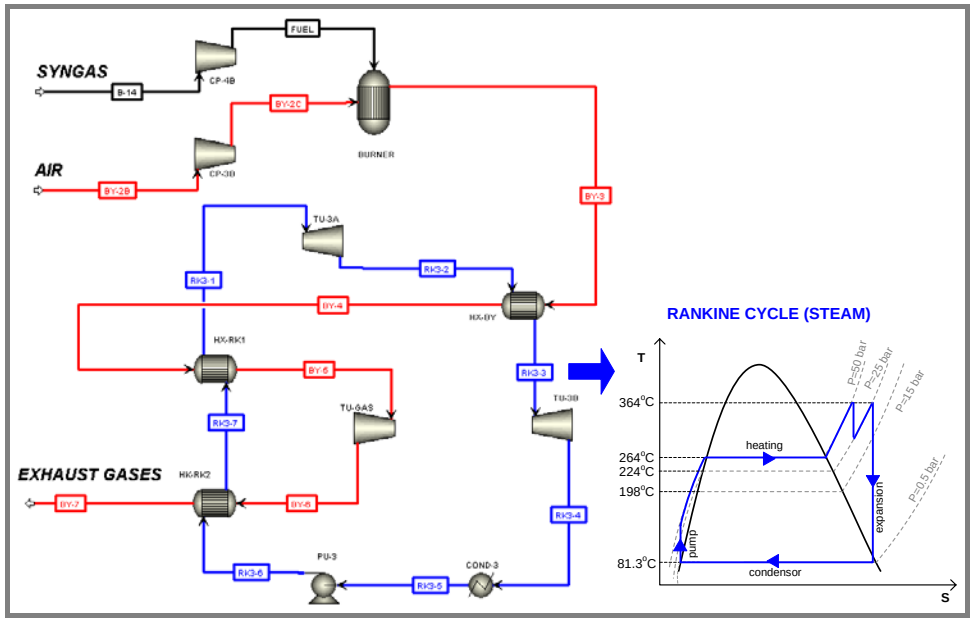


Figure 4.14. Simulation of the combined Brayton-Rankine cycle for electricity production, and its corresponding T-s diagram.

Table 4.18. Gas Turbine (in a IGCC) specifications for trace elements in a product gas [105]

Element	Maximum concentration	Potential failures
Potassium	< 1ppm	Hot corrosion
Sodium	< 1ppm	Hot corrosion
Lead	1 ppm	Hot corrosion
Zinc	1 ppm	Fouling
Tar	< 0.5 mg/m^3	Hot corrosion
Particles	< 0.1 ppm	Fouling

Maintenance of the gas turbine is critical for the performance of the IGCC process. The lifetime of the turbine can be shortened due to erosion and high temperature corrosion caused by particles impact and impurities present in the flue gas such as alkali metals. Table 4.18 summarizes the maximum tolerable concentrations set by the turbine manufacturers. This limitations are taken into account in the cleaning stages of our simulations.

5. BIOFUELS APPLICATION

As shown in Figure 5.1, biofuels have many applications as energy carriers, notably heat, electricity, transport fuels and chemicals production. Second generation biofuels obtained through thermochemical (e.g., SNG, methanol, Fischer-Tropsch fuels, and hydrogen) can be used in a wider range of applications than the fuels obtained via biochemical conversion. In fact, bioethanol and biodiesel are almost limited to the transportation sector. Moreover, thermochemical-based fuels have higher octane and cetane numbers, which is preferable when blending with gasoline or diesel (see Table 5.3). Methane produced from anaerobic digestion (biogas) can be applied in similar purposes as thermochemically obtained methane (SNG). However, biogas requires more wet streams and the production scale is smaller.

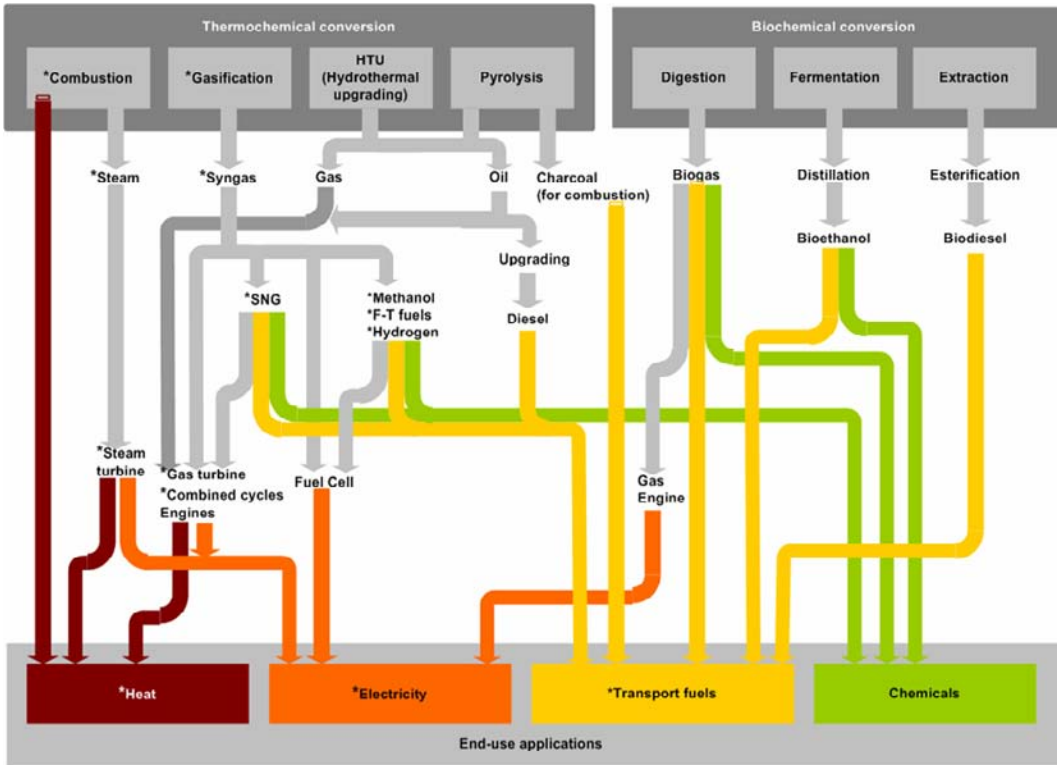


Figure 5.1. Main applications of biofuels obtained via thermochemical and biochemical conversion methods. Names marked with an asterisk (*) indicate the biofuels and processes covered in this paper.

The biofuels selected for this paper are second generation biofuels obtained through gasification and further catalytic conversion. These biofuels are SNG, methanol, Fischer-

Tropsch fuels, and hydrogen as well as heat and electricity generation. Next sections give a more detailed information about their end application in the market.

5.1. Electricity Generation

5.1.1. Combined Cycles IGCC

As shown in section 4.9, the IGCC concept is based on the combination of a gasification system with a combined cycle consisting of a gas turbine and a steam cycle. The advantage of incorporating a gasifier is to convert solid and liquid residual fuels into a form that gas turbines can accept. Currently, this concept offers the highest electrical efficiencies in thermochemical conversion of biomass. Although the two main components of an IGCC (gasification and gas turbines) are both mature coal technologies, their integration is relatively new. Efficiencies of the best first-generation plants are all below 45%. Higher efficiencies are expected for a better integrated systems which should also incorporate more advanced gas turbines. However, assuming that the gasification and combined cycles efficiencies are around 80% and 60% respectively, the overall IGCC efficiency is limited to 48-50%. Figure 5.2 schematically shows the principle of a Biomass IGCC system.

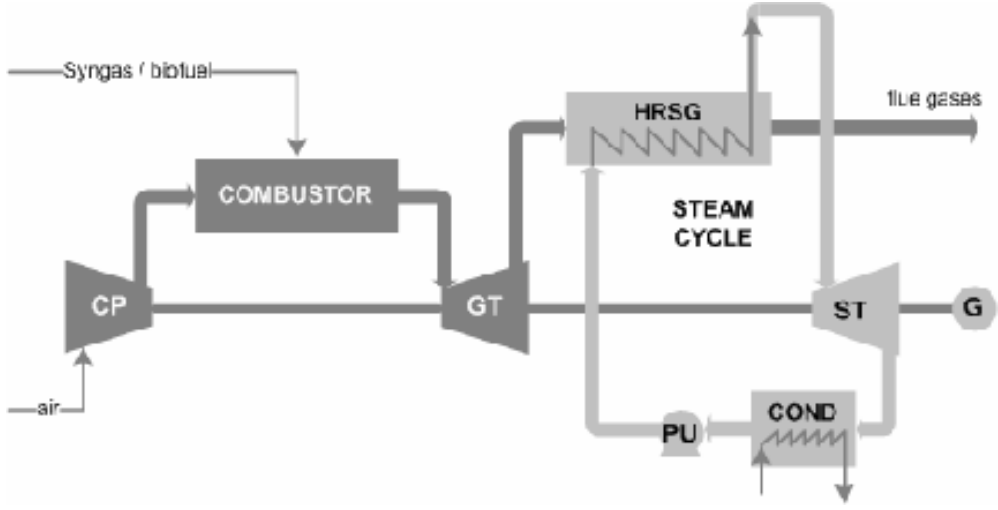


Figure 5.2. Schematic block diagram showing the main section of a biomass IGCC, where CP=compressor, GT=gas turbine, ST= steam turbine, HRSG=heat recovery steam generation, PU=pump, G=generator and COND= condenser.

5.1.2. Fuel Cells

Another approach that is gaining interest for electricity generation is the combination of gasification with fuels cells. The potential applications of fuels cells can be found in stationary power plant, portable power generators or even in power sources for vehicles. A fuel cell is an electrochemical device that produces electricity from the chemical energy stored in a fuel (e.g., hydrogen, methane, methanol, gasoline, etc) and an oxidant (mainly oxygen). Unlike a electrochemical cell batteries, fuel cells does not run down or require

recharging. They will produce electricity and heat as long as fuel and an oxidizer are supplied. Fuel cell construction generally consists of a fuel electrode (anode) and an oxidant electrode (cathode) separated by an ion-conducting membrane (electrolyte), which separates the two reactants from mixing together and allows internal transport of the ions. Fuel cells are classified by their electrolyte material.

Figure 5.3 schematically shows the principle of a Proton Exchange Membrane (PEM) fuel cell. As shown, electricity is generated by a simple electrochemical reaction in which the oxidizer (cathode) and the fuel (anode) combine to form a product (typically H_2O for H_2 fuel cells) and heat. In the anode side, the hydrogen diffuses to the hydrogen catalyst where it later dissociates into protons and electrons.

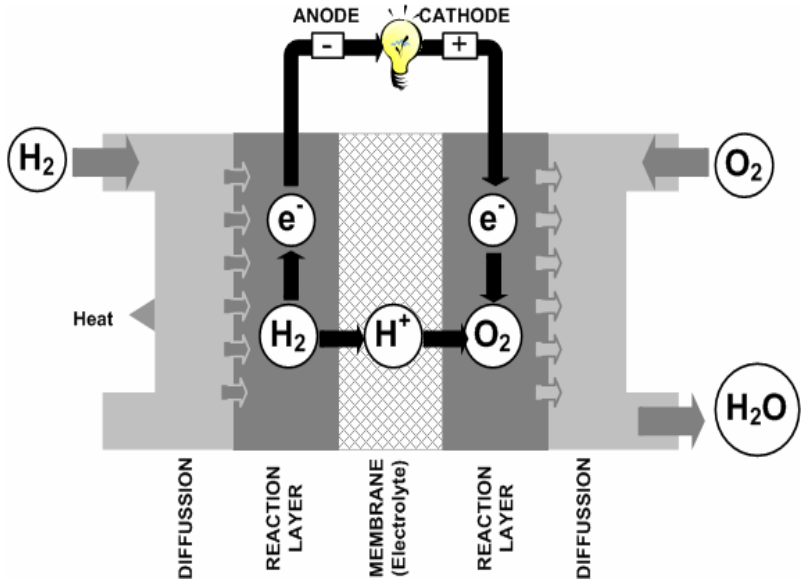


Figure 5.3. Schematic representation of the principle of a PEM fuel cell.

Protons pass then through the ion-conducting membrane (electrolyte) to the oxygen cathode catalyst, whereas the electrons pass through an external electrical circuit as a Direct Current (DC) to power useful devices. At the oxygen cathode, oxygen molecules react with the coming protons and electrons. The reactions taken place in a PEM fuel cell are:

$$\textit{Anode Reaction: } 2H_2 \Rightarrow 4H^+ + 4e^- \tag{41}$$

$$\textit{Cathode Reaction: } O_2 + 4H^+ + 4e^- \Rightarrow 2H_2O \tag{42}$$

$$\textit{Overall Cell Reaction: } 2H_2 + O_2 \Rightarrow 2H_2O \tag{43}$$

Individual fuel cells can then be combined into a fuel cell "stack." The number of fuel cells in the stack determines the total voltage, and the surface area of each cell determines the total current. The total electrical power (W) is the voltage (V) times the current (I_N), as follows:

$$W = V \times I_N \tag{44}$$

Fuel cells can be poisoned by different types of compounds. Table 5.1 summarizes the limit concentration of main poisoning compounds as well as the compounds that are considered fuels.

Table 5.1. Inlet gas purity requirements for various Fuel Cells systems [82]

Compound	PEM: Proton Exchange Membrane	Alkaline	Phosphoric Acid	MCFC: Molten Carbonate	ITSOFC: Intermediate Temperature	TSOFC: Tubular Solid-Oxide
H_2	Fuel	Fuel	Fuel	Fuel	Fuel	Fuel
CO	Poison	Poison	Poison	Fuel	Fuel	Fuel
CH_4	Diluent	Poison	Diluent	Diluent	Fuel	Fuel
CO_2 and H_2O	Diluent	Poison	Diluent	Diluent	Diluent	Diluent
H_2S and COS	(no data)	Poison	Poison <50 ppm	Poison <0.5 ppm	Poison	Poison <1 ppm
Halogens (HCl)	(no data)	Poison	Poison	Poison <1 ppm	(no data)	Poison <1 ppm
Alkali metals	(no data)	(no data)	(no data)	Electrolyte loss 1-10ppm	(no data)	(no data)

Because of the differences in electrolytes, operating temperatures, catalysts and other factors, the same compound can behave differently in other fuel cells. Nevertheless, the major poisons for all types of fuel cells are sulfur-containing compounds such as hydrogen sulfide (H_2S) and carbonyl sulfide (COS). Sulfur compounds are naturally present in all fossil fuels, and small quantities remain after normal processing and must be almost completely removed before entering the fuel cell. Precisely, in the case of biomass gasification, sulfur compounds are removed in cleaning stages by absorption with a MDEA solution (see section 4.3).

Unlike IGCC, fuel cells do not operate thermal cycles and, hence, they are not constrained by thermodynamic limits such as the Carnot cycle efficiency. However, thermodynamic laws also apply in chemical process like fuel cells, but the maximum theoretical efficiency is higher, i.e., 83% for a hydrogen fuel cell operating a 25 °C [106]. Although this number is considerably higher than for the case of a Otto cycle thermal machine (i.e., 60% for a compression ratio of 10 and specific heat ratio of 1.4), real efficiencies of complete conversion chains can be lower. This is the case for propulsion, where electrical energy obtained from the fuel cell still has to be converted into mechanical power with the corresponding efficiency losses.

Hydrogen is one of the bests fuel to apply in a fuel cell system, leading to the highest efficiency. However, hydrogen is very difficult to store in either gas or liquid state. Chemical storage of hydrogen in liquid fuels is considered to be an interesting alternative, especially for mobile applications [107]. In this case, several processes are required prior a fuel cell system such as steam reforming or catalytic partial oxidation and further cleaning stages. Fuels such as methanol, formic acid or medium-size chain hydrocarbons can be also fed directly without any previous processing. However, the corresponding fuel cell performance is still not satisfactory enough due to the inherent CO production (i.e., from incomplete oxidation) and lower power density and efficiency. CO adsorbs onto the platinum catalyst, reducing the

surface area and, hence, the performance of the fuel cell. Reactions (45-47) occurs in a direct methanol fuel cell (DMFC):

$$\textit{Anode Reaction: } CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad (45)$$

$$\textit{Cathode Reaction: } (3/2)O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad (46)$$

$$\textit{Overall Cell Reaction: } CH_3OH + (3/2)O_2 \rightarrow CO_2 + H_2O \quad (47)$$

Table 5.2 compares the main characteristics and efficiencies obtained in different fuel cells systems. As mentioned, DMFC are still less efficient than reformed methanol fuel cells.

Table 5.2. Characteristics and efficiencies of several fuel cells

Parameter ➡ Fuel Cell ⬇	Electrolyte	Working temperature	Electrical efficiency	Estimated power
PEM	e.g.Nafion or PBI[(a)]	25-220°C	cell: 50-70% system: 30-50%	100W-500kW
Alkaline	Alkaline (aq) solution	<80 °C	cell: 60-70% system: 52%	10kW-100kW
Phosphoric Acid	Molten H_3PO_4	150-200°C	cell: 55% system: 40%	<10MW
MCFC	e.g., molten $NaHCO_3$	600-650°C	cell: 55% system: 47%	100MW
TSOFC	e.g. Y_2O_3-stabilized ZrO_2	850-1100°C	cell: 80% system: 70%	<100MW
DMFC (methanol)	Polymer membrane	90-120°C	cell: 20-30% system: 10-20%	100kW-1MW
Reformed methanol fuel cell	Polymer membrane	125-200°C	cell: 50-60% system: 25-40%	5W-100kW

(a) PBI: Polybenzimidazole fiber.

5.2. Heat and/or Steam Generation

Traditionally, direct combustion of biomass has been used to generate heat for many applications (see Figure 5.4 case (A)). Alternatively, heat can also be produced by burning the syngas obtained after gasification in a combustion chamber (see Figure 5.4 case (B)). Another part of heat is recovered from syngas cooling prior to cleaning stages. Using produced syngas in heat applications is comparable to two-stage-combustion, with the difference that the gasifier and the combustor are physically separated. The main advantages of the gasification/combustion route compared with the direct combustion are as follows:

- Low overall air excess factors, allowing relatively high efficiencies.
- Low levels of SO_x and NO_x emissions. Apart from environmental concerns, cleaning syngas prior to combustion results on considerable cost savings as the volume flow rate of syngas is roughly 50% lower than the volume of exhaust gases.

- Less fouling of heat exchangers or other heating systems due to less fly ash in the combustion gases.

However, one of the disadvantages of the gasification/combustion cycle is the possible heat loss during gasification and transport piping. Hence, the system needs to be carefully insulated to minimize heat losses as well as tar condensation.

Another alternative for heat generation is the so-called Combined Heat and Power (CHP) concept. Unlike conventional power plants where the heat remaining after electricity generation is destroyed in cooling towers or emitted as flue gases to the environment, CHP plants makes use of this by-product heat for domestic or industrial applications. For instance, in Scandinavia and Eastern Europe, hot water is produced for district heating at temperatures ranging from 80 to 130°C. Fryda et al [108] calculated an exergetic efficiency (Ψ_{ex}) of 36% for a CHP system, integrating an allothermal steam-blown fluidized gasifier with a SOFC fuel cell.

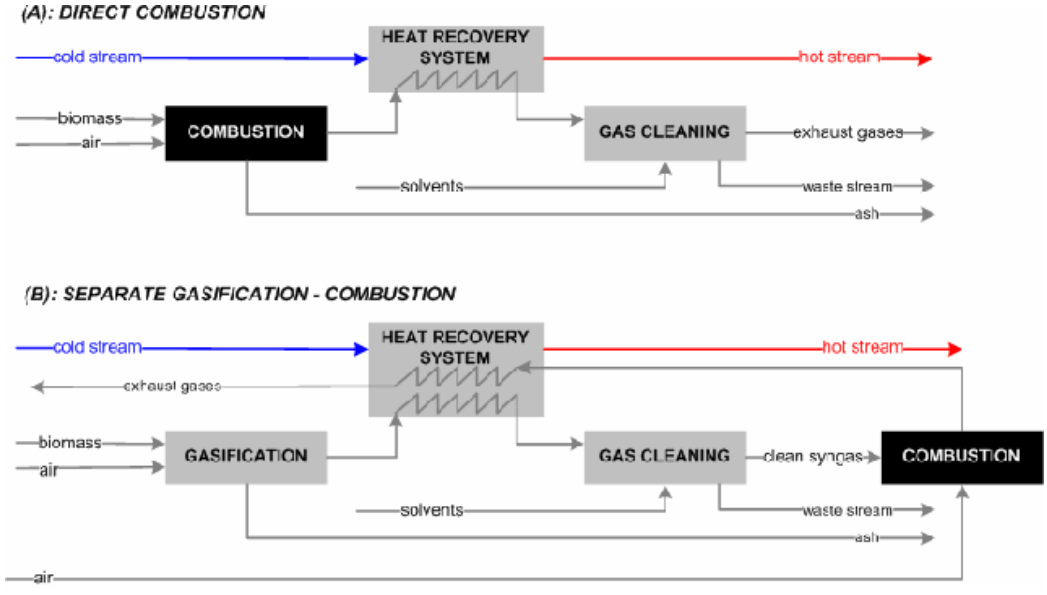


Figure 5.4. Comparison of traditional biomass combustion (A), with 2 stage gasification + combustion (B).

5.3. Transport Fuels (Synfuels)

Nowadays, the transport section is almost exclusively fueled by fossil sources, accounting for an important share of global CO_2 emissions. Consequently, energy policies of some industrialized countries have established that biofuels should partly replace the use of fossil fuels in transport. Therefore, the key issue is to determine which biofuels are more appropriate for this transition. As shown in Table 5.3., thermochemical-based fuel have higher octane and cetane numbers, which is preferable when blending with gasoline or diesel.

Table 5.3. Some biofuels properties . Higher values for LHV, octane number and cetane number are desirable

Technology	Fuel	Specific gravity	(a) LHV (MJ/Kg)	(b) Octane number	(b) Cetane number
Biochemical conversion	Bio-Ethanol	0.79	27.0	109	-
	Bio-Diesel	0.89	37.0	-	55
	Buthanol	0.81	36.0	96-105	-
Thermochemical conversion	Mixed Alcohols	0.8	27-36	96-109	-
	Methane	0.42	49.5	>120	-
	Methanol	~0.80	20.1	109	-
	Fischer-Tropsch	0.77	43.9	-	74.6
	Hydrogen	0.07	120.0	>130	-
	DME	0.66	28.9	-	>55
Petroleum refineries	Gasoline	0.72-0.78	43.5	91-100	-
	Diesel	0.85	45.0	-	37-56

Experts from the Institut für Energetik und Umwelt (Leipzig, Germany) have conducted a study to determine biofuels feasibility in the current fuel distribution system and vehicle fleet (see Table 5.4) [109]. They have compared 5 different thermochemically-derived biofuels and concluded that Fischer-Tropsch diesel has the highest potential for their immediate implementation. In fact, Fischer-Tropsch diesel could be readily used in standard diesel engines with similar performances as fossil diesel or biodiesel.

SNG is advantageous in terms of production efficiency and GHG's emissions, but current distribution infrastructure and vehicle fleet are not widely adapted yet. Same barriers applies for the DME but to a larger extent. Hydrogen is comparatively expensive and it also has to overcome similar technical barriers. In particular, major concerns of SNG and hydrogen application are derived from the need of high pressures in the filling stations, i.e., 250-350 and 700 bar, respectively.

Table 5.4. Comparison of technology and market potential of 5 thermochemically-based biofuels. Adapted from [109]

Biofuel	Biofuel production		Biofuel feasibility	
	Overall thermal efficiency	Technical effort (complexity)	Current fuel distribution	Current vehicle fleet
FT-Diesel	Medium	Low	High	High
Methanol	Medium	Medium	Medium	Low
SNG	High	High	Medium	Medium
Hydrogen	High	High	Low	Low
DME	Medium	Low	Low	Low

In Lille (France), some public buses are already powered by compressed CNG at 250 bar, whereas in the Netherlands, CNGNet is implementing around 50 tank stations all over the country. Moreover, Linde has created the world's first hydrogen filling station using 700 bar

technology for the Adam Opel AG, which represent an important milestone in the course of an hydrogen-powered car society.

On the other hand, methanol can be mixed with gasoline up to 10% in ICE vehicles without adjustments to the motor or fuel system. However, pure methanol cannot be injected in modern petroleum cars without modification, due to potential damage to metal piping and rubber seals. Adapted Flexible Fuel Vehicles (FFV's) can run on any blend of M85 and gasoline, but their use has been limited mainly to demonstration projects and small government fleets, particularly in California. A possible better alternative for the near future, would be the use of pure methanol in fuel cell cars, although this technology is still under development.

Several authors have also compared the efficiency of producing and using several first and second generation biofuels for 4 cases: (1) conventional ICE cars, (2) hybrid cars, (3) fuel cell cars, (4) electric cars. Comparison of these systems is presented in Table 5.5 [110-112].

According to these values, it seems that hybrid cars would be the most efficient solution for vehicles powered by fossil fuels, whereas for the case of using biofuel, Sterner et al suggest that electric cars results on higher efficiencies and lower CO_2 emissions [111]. However, prices for both hybrid and electric cars are still considerably higher than conventional ICE cars.

Table 5.5. Well-to-wheel efficiency of different fossil fuels and biofuels powered vehicles

Well-to-Wheel efficiency	Conventional (ICE)	Hybrid cars (HEV)	Fuel cell (FC)	Electric (BEV)
Fossil fuels [110, 112]				
Natural gas	16-19%	32%	25%	35%
Gasoline	14%	27%	-	-
Diesel	17%			
FT diesel	19%	30%	-	-
FT diesel - gas mix	22%	32%	-	-
Methanol	-	-	16%	-
Steam reformed H_2	13-14%	22%	26-28%	-
Electrolyzed H_2	-	-	13%	-
Battery	-	-	-	21%
Biofuels [111]				
Rapeseed-to-biodiesel (a)	6%	-	-	9%
Wood-to-Fischer Tropsch (b)	10%	-	-	35%
Maize-to-biogas (a)	24%	-	-	24%

5.4. Chemicals

Another application of biofuels is the production of different chemicals by further processing. Figure 5.5 indicates the main chemicals obtained through common processes. However, this application is out of the scope of this chapter.

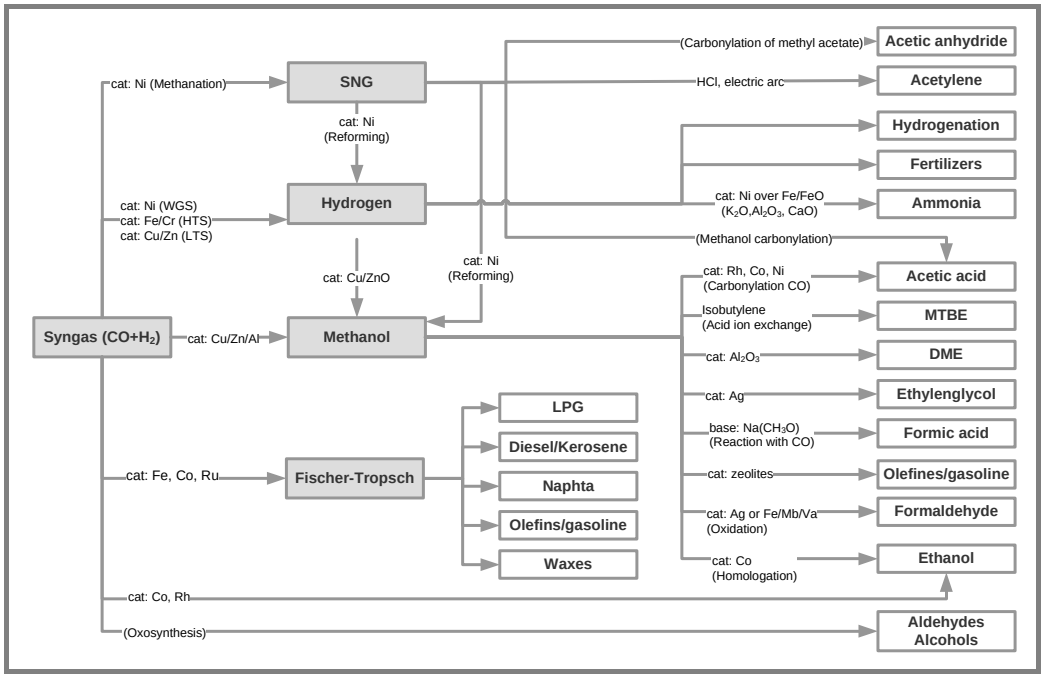


Figure 5.5. Different route to produce chemicals from syngas and other biofuels.

6. Efficiency Evaluation of Different Biofuel Processes

As aforementioned in section 1.4, the aim of this chapter is to present the results obtained from the efficiency evaluation of 5 biowaste-to-biofuels conversion routes. In literature, there are several definitions used to evaluate the energy efficiency of any process, although the most commons expressions are based on high heating values (HHV) and exergy concept. In general, energy efficiency can be defined as the ratio of energy production divided by energy consumption, where the differences among analyses lay on the way of calculating both concepts (see section 6.2.2 and 6.2.4).

In some cases, both analyses are also accompanied with a mass conversion yield calculation as it gives a rough estimation about the amount of biowastes that are converted to biofuels, i.e., kg biofuel/kg biowastes (see section 0). Different analyses are here presented chronologically, i.e., from early definitions founded in literature to more recent exergetic efficiency, and the corresponding results are later compared. Our motivation for comparing these different approaches is that one tool alone does not give enough information to draw conclusions. All the analyses start from the mass and energy balances obtained from simulations in Aspen Plus [56], whereas boundary conditions are similar to those presented in section 4.1.

6.1. Mass and Energy Balances

Mass and energy balances verify whether all the flows have been included and balanced, and they are also needed for later mass conversion, energy efficiency and exergy analysis. In a steady state process, the mass balance for a unit or a control region can be written as:

$$\sum_i m_{i,inlet} - \sum_j m_{j,outlet} = 0 \tag{48}$$

where m_i and m_j represent the mass flow of inlet and outlet streams respectively. Similarly, the energy balance of a control region can be described with the following expression derived from the 1st Law of Thermodynamics, which applies for the principle of energy conservation in a closed control region:

$$\left(Q_{in} - Q_{out}\right) + \left(W_{in} - W_{out}\right) + \sum_i m_i \cdot \left(h + \frac{c^2}{2} + gz\right)_i - \sum_j m_j \cdot \left(h + \frac{c^2}{2} + gz\right)_j = 0 \tag{49}$$

where Q_{in}, Q_{out}, W_{in} and W_{out} are heat and work inlet and outlet flows respectively. Specific enthalpy, kinetic and potential energy associated of mass flows entering and leaving the system are represented by *h*, *c* and *z* symbols, and gravity by *g*. Kinetic and potential energy contribution can be neglected, leaving the energy balance as:

$$\left(Q_{in} - Q_{out}\right) + \left(W_{in} - W_{out}\right) + \sum_i m_i \cdot h_i - \sum_j m_j \cdot h_j = 0 \tag{50}$$

As an example, results of mass and energy balances for SNG production from wood wastes (i.e., stream A of Table 6.3) are shown in Table 6.1. Same procedure has been applied for the rest of biowastes streams and biofuels production chains.

Table 6.1. Mass and energy balances for SNG production from wood wastes (stream A)

Biofuel	Mass balance				Energy balance [(a)]			
	Inlet streams (kg/h)		Outlet streams (kg/h)		Input (MW)		Output (MW)	
	Stream	Value	Stream	Value	Stream	Value	Stream	Value
SNG	Biomass	57,000	Biofuel: SNG	14,647	Biomass	-94.4	Biofuel: SNG	-18.2
	Utilities	⇩	Ash	1,975	Utilities	⇩	Ash	0.8
	>Air	70,000	CO_2 product	17,450	>Air	0	CO_2 product	-42.5
	>H_2O process	34,527	Exhaust gases	74,837	>H_2O process	-151.8	Exhaust gases	-43.3

Table 6.1. (Continued)

	Mass balance				Energy balance [a]			
	Inlet streams (kg/h)		Outlet streams (kg/h)		Input (MW)		Output (MW)	
SNG					>H_2O cooling[b]	-138.0		
	Solvents	152,876	Waste water	197,635	Solvents	-567.0	Waste water	-812.9
			Extra steam	7,859			Extra steam	-27.9
					Q_{in}	119.7	Q_{out}	96.1
					W_{in}	19.7	W_{out}	16.4
	Total	314,403	Total	314,403	Total	-831.5	Total	-831.5

(a) Calculated according to reference state in Aspen Plus.
(b) Calculated as differences of enthalpy of cool water minus hot water.

6.2. Efficiency

6.2.1. Mass Conversion Yields

Although the mass conversion yield (μ) calculation is not accurate enough to make final decisions, it gives an idea about the amount of biowaste that has been converted to biofuel. This coefficient is here defined as follows:

$$\mu = \frac{m_{biofuel}}{m_{biowaste}} \times 100 \tag{51}$$

where $m_{biofuel}$ and $m_{biowastes}$ are the mass flows (kg/h) of the biofuels and wet biowastes respectively. For all the cases, biowastes flow rate is fixed to 57,000kg/hr and biofuels quality is also equalized among biowastes. For instance, for the case of SNG production, the Wobbe index of the formed biofuels is set to 43.5 MJ/Nm^3, except for the case of stream D that needed further nitrogen separation in order to reach this target. Hence, the corresponding $\mu_{methane}$ and μ_{SNG} values of the stream D would be slightly lower than 9% and 11%. The rest of biowaste-to-biofuels routes meet the specifications. Results from those calculations are presented in the Table 6.2.

As observed, methanol production results on the highest mass conversion yield, irrespectively of the biowaste being consumed. SNG is the second best alternative followed by Fischer-Tropsch production. Conversely, the lowest yields are obtained for the hydrogen chain. In terms of biowaste selection, woody wastes (stream A) followed by agriculture (stream C) and municipal wastes (stream E) seems to be more convenient due to their higher carbon and hydrogen content.

Table 6.2. Mass yield conversion of each biowaste stream for 4 different biofuels

Mass conversion yield (η)	Symbol	Stream A	Stream B	Stream C	Stream D	Stream E
Methane SNG (~74 – 80 mol%)	$\mu_{methane}$ μ_{SNG}	21% 26%	11% 13%	16% 20%	9% 11%	13% 17%
Methanol	$\mu_{methanol}$	48%	27%	33%	16%	32%
Fischer-Tropsch	$\mu_{Fischer}$	18%	12%	16%	8%	12%
Hydrogen	$\mu_{hydrogen}$	9%	6%	7%	7%	6%
Heat-Electricity	$\mu_{electricity}$	-	-	-	-	-

6.2.2. Efficiency Based on HHV and LHV of Biowastes and Biofuels

Similarly to the cold gas efficiency of a gasifier, η_{LHV} is defined by Eq. (52) as the stored energy in the *cold gas product* divided by the stored energy in the *raw feedstock*. In some analyses, HHV is preferred over LHV reference as for many applications, such as oxidation reactions with air, energy carriers has to be based on the true energy content (i.e., HHV) rather than on the LHV [113]. The HHV of a fuel (also known as the gross calorific value or high heating value) is defined as the amount of heat released by a fuel once it is combusted and all the products have returned to a temperature of 25 °C. The difference between HHV and LHV is caused by the heat of evaporation of the water formed from the hydrogen present in the material and in the moisture. After the corresponding cleaning stages, biofuels still contain small quantities of other compounds, i.e., unreacted syngas. Hence, the corresponding $HHV_{biofuel}$ and $LHV_{biofuel}$ are calculated as a mixture of compounds:

$$\eta_{HHV} = \frac{m_{biofuel} \cdot HHV_{biofuel}}{m_{biowaste} \cdot HHV_{biowaste}} = \frac{\sum_j m_j \cdot HHV_j}{m_{biowaste} \cdot HHV_{biowaste}} \tag{52}$$

$$\eta_{LHV} = \frac{m_{biofuel} \cdot LHV_{biofuel}}{m_{biowaste} \cdot LHV_{biowaste}} = \frac{\sum_j m_j \cdot LHV_j}{m_{biowaste} \cdot LHV_{biowaste}} \tag{53}$$

Table 6.3 summarizes the HHV values of the biofuels and minor compounds present in the calculations of the HHV efficiency (η_{HHV}).

As in Phyllis database [33], Milne Equation is used to calculate $HHV_{biowastes}$ (see Table 6.3). Results obtained from our analysis (η_{HHV} and η_{LHV}) are tabulated in Table 6.8, where calculations based on LHV values are done by replacing HHV in the Eq.(52).

For the case of heat and electricity production, the numerator term (i.e., $m_{biofuel}.HHV_{biofuel}$) of the Eqs.(52-53) is substituted by the electricity (MW_e) and heat (MW_{th}) produced It should be notice, however, that boundary conditions found in literature are frequently different than the conditions adopted here, and, hence, it complicates comparison. Moreover, composition of the biowastes, which normally consists of woody wastes (stream A), also differs in each study.

Table 6.3. HHV of different compounds present in the biofuels produced from biowastes

Compound	HHV (MJ/kg)	Compound	HHV (MJ/kg)	Compound	HHV (MJ/kg)
H_2	141.9	C_7H_{16}	48.5	$C_{16}H_{34}$	47.3
CO	10.9	C_8H_{18}	48.3	$C_{17}H_{36}$	47.3
CH_3OH	22.7	C_9H_{20}	47.9	$C_{18}H_{38}$	47.3
CH_4	55.5	$C_{10}H_{22}$	47.7	$C_{19}H_{40}$	47.2
C_2H_6	51.9	$C_{11}H_{24}$	47.6	$C_{20}H_{42}$	47.2
C_3H_8	50.4	$C_{12}H_{26}$	47.6	$C_{21}H_{44}$	47.2
C_4H_{10}	49.5	$C_{13}H_{28}$	47.5	$C_{22}H_{46}$	47.1
C_5H_{12}	49.1	$C_{14}H_{30}$	47.4	$C_{23}H_{48}$	47.1
C_6H_{14}	48.7	$C_{15}H_{32}$	47.4	$C_{24}H_{50}$	47.1

6.2.3. Overall Energy Efficiency

For the calculation of the overall energy efficiency (i.e., ratio of total energy produced divided by total energy consumed), electricity and thermal energy consumption rates are also included in the equations. In some cases, electricity is also produced within the process, which increases the output term (numerator) of the overall energy efficiency equations:

$$\Psi_{HHV} = \frac{m_{biofuel} \cdot HHV_{biofuel} + W_{output} + Q_{output}}{m_{biowaste} \cdot HHV_{biowaste} + W_{input} + Q_{input}} \tag{54}$$

$$\Psi_{LHV} = \frac{m_{biofuel} \cdot LHV_{biofuel} + W_{output} + Q_{output}}{m_{dry\,biowaste} \cdot LHV_{biowaste} + W_{input} + Q_{input}} \tag{55}$$

Results obtained from our analysis are presented in Table 6.4, whereas values found in literature are presented in subsequent Table 6.5. However, it is difficult to make a straight comparison as values found in literature correspond to processes that may have different operational conditions, different designs and integration of the operation units, as well as different wood composition. In general, SNG process achieves the highest efficiencies in most of the studies.

Table 6.4. Comparison of overall energy efficiency (Ψ_{HHV} and Ψ_{LHV}) for different biofuels and biowastes

Biofuel	Parameter	Stream A	Stream B	Stream C	Stream D	Stream E
SNG	Ψ_{HHV} (Ψ_{LHV})	72 (69)%	70 (68)%	71 (68)%	65 (63)%	69 (67)%
Methanol	Ψ_{HHV} (Ψ_{LHV})	69 (67)%	64 (62)%	64 (62)%	61 (60)%	64 (62)%
Fischer- Tropsch	Ψ_{HHV} (Ψ_{LHV})	67 (66)%	67 (66)%	69 (68)%	65 (64)%	64 (63)%
Hydrogen	Ψ_{HHV} (Ψ_{LHV})	66 (61)%	66 (61)%	67 (61)%	66 (61)%	65 (60)%
Heat and Electricity	Ψ_{HHV} (Ψ_{LHV})	46 (48)%	46 (48)%	47 (49)%	43 (46)%	44 (47)%

Table 6.5.Comparison of Ψ_{HVV} and Ψ_{LHV} for the case of wood wastes (stream A) with values found in literature

Analysis	Parameter	Synthetic Natural Gas (SNG)	Methanol	Fischer-Tropsch	Hydrogen	Heat and Electricity
Our case (stream A)	Ψ_{HHV} (Ψ_{LHV})	72 (69)%	69 (67)%	67 (66)%	66 (61)%	46 (48)%
Literature values (wood)	Ψ_{HHV} (Ψ_{LHV})	70(67)% [20, 21] 60% [15] 60-65%[22] 65% [9] 58% [12]	52-59%[13] 54-58%[14] 40-52%[9] 50-54%[12] 45% [11]	42% [15] 40-52%[9] (53%) [16] 40-45%[17] 33-50%[18] 56% [19]	56-74%[13] 56-64%[14] 45%[11]	39-43%[103] (38-44)%[114] 32% [4] 35-40%[63]

6.2.4. Exergetic Efficiency

Energy and exergy analyses are used to evaluate and compare the thermodynamic performance of different systems. The previous *overall energy efficiency analysis* (section 0) is based on the first law of Thermodynamics, which is only concerned with energy conservation and treats all forms of energy as equivalent. On the contrary, energy can be divided in two different forms of energy, i.e., ordered and disordered. According to Kotas [115], *disordered energy* is characterized by entropy, it has a variable quality and it depends on the form of energy (e.g., thermal, chemical, etc) and on the parameters of the energy carrier and the reference environment. The same author defines *ordered energy* as not being characterized by entropy, having invariant quality and being fully convertible, through work interaction, to other forms of energy. For instance, thermal energy is disordered and mechanical is ordered, and the same amount of these two energy forms will provide different amount of work. Therefore, an energy analysis only based on the 1st law of thermodynamics does not take into account losses on the quality of the energy, which is a key factor when evaluating and optimizing the thermodynamic performance of a system.

Unlike the traditional energy efficiency methods, *exergy* is based on the first and second law of Thermodynamics and it considers that, although energy cannot be created or destroyed, it can be degraded in quality. Hence, exergy can be defined as the maximum amount of work that can be produced by a system when it is brought into equilibrium with a reference state, which is defined at standard temperature (T_o=25^{o}C) and pressure (P_o=1bar), and the system of reference species covering all chemical elements. Some reference species include CO_2, O_2 and N_2, having a mole fraction of 0.003, 0.2099, 0.7903 in dry air, respectively.

The usefulness of an exergy analysis is that it determines how much potential work is lost during a process and it helps to identify and allocate the main losses. For example, an exergy analysis can be applied to minimize the use of natural resources. Hence, and in agreement with other authors [23, 24], we propose exergy analysis as a more accurate method to evaluate the thermodynamic performance of a system or process. The main components of exergy are the *kinetic*, *potential*, *physical* and *chemical exergy*. Kinetic and potential exergies are expressed by the kinetic and potential energy calculated in relation to the reference environment and they can be neglected when calculating the exergy content of a process stream. Hence, the two forms of exergy being important are the physical and chemical.

6.2.4.1. Chemical Exergy

Chemical exergy is defined at the reference state and it results from the deviation of composition in comparison with the components commonly existing in the reference state. The specific chemical exergy of a compound *($\varepsilon_{ch,i}$)* is obtained from tabulated values of Szargut *et al*. [116]. Streams of any chemical processes commonly consists of a mixture of different compounds and the corresponding chemical exergy *($\varepsilon_{ch,mix}$)* can be calculated as follows:

$$\varepsilon_{ch,\,mix} = \sum_i x_i \cdot \varepsilon_{ch,i} + RT_o \sum_i x_i \cdot \ln(x_i) \tag{56}$$

where x_i is the molar fraction of a compound, R is the universal gas constant and T_o is the reference temperature, which is set to 25°C in our analyses. The last part of the equation is identical to the specific Gibbs energy of mixing *(Δg_{mix})*:

$$\Delta g_{mix} = RT \sum_i x_i \cdot \ln(x_i) \tag{57}$$

The previous Eq. (56) can be applied to calculate the chemical exergy of standard pure chemical compounds. However, these equations are not useful for more complex compounds such as biomass or wastes. In this case, chemical exergy of biowastes *($\varepsilon_{ch,biowaste}$)* is calculated from the statistical correlation (β) by the same author [116]:

$$\varepsilon_{ch,biowaste} = z_{org}\left(\beta \cdot LHV_{org}\right) + z_S\left(\varepsilon_{ch,S} - C_S\right) + z_{water} \cdot \varepsilon_{ch,water} + z_{ash} \cdot \varepsilon_{ch,ash} \tag{58}$$

where z_{org} is the organic mass fraction of biowastes, and z_S, z_{water} and z_{ash} are the mass fraction of sulphur, water and ash respectively. LHV_{org} is the LHV of the organic fraction and it is calculated from the Milne equation of the HHV by only considering the organic fraction [33]. The coefficient β is defined as ratio of the chemical exergy to the LHV_{org}, and can be calculated from atomic ratios of oxygen, hydrogen and nitrogen depending on the biowaste stream as follows:

$$\beta = \frac{1.0412 + 0.2160 \cdot \left(\frac{z_{H_2}}{z_C}\right) - 0.2499 \cdot \left(\frac{z_{O_2}}{z_C}\right)\left[1 + 0.7884 \cdot \left(\frac{z_{H_2}}{z_C}\right)\right] + 0.0450 \cdot \left(\frac{z_{N_2}}{z_C}\right)}{1 - 0.3035 \cdot \left(\frac{z_{O_2}}{z_C}\right)} \quad \textit{(for stream A)} \tag{59}$$

$$\beta = \frac{1.044 + 0.0160 \cdot \left(\frac{H}{C}\right) - 0.3493 \cdot \left(\frac{O}{C}\right)\left[1 + 0.0531 \cdot \left(\frac{H}{C}\right)\right] + 0.0493 \cdot \left(\frac{N}{C}\right)}{1 - 0.4124 \cdot \left(\frac{O}{C}\right)} \quad \textit{(for streams B, C, E)} \tag{60}$$

$$\beta = 1.0407 + 0.0154\left(\frac{H}{C}\right) + 0.0562\left(\frac{O}{C}\right) + 0.5904\left(\frac{S}{C}\right) \cdot \left(1 - 0.175\left(\frac{H}{C}\right)\right) \quad \textit{(for stream D)} \tag{61}$$

6.2.4.2. Physical Exergy

Physical exergy represents the energetic value due to deviation of temperature and pressure from the reference environment. The specific physical exergy of a compound $(\varepsilon_{ph,i})$ is calculated using enthalpy (h) and entropy (s) data for a given system:

$$\varepsilon_{ph,i} = \Delta h - T_o \Delta s = (h - h_o) - T_o (s - s_o) \tag{62}$$

where h_o and s_o is the enthalpy and entropy at the reference state (i.e, 25°C and 1 bar). The enthalpy and entropy are calculated from the specific heat capacity (C_p) of a compound. When the specific heat capacity (C_p) is dependent on the temperature, Eq.(62) is rewritten as follows.

$$\varepsilon_{ph,i} = \int_{To}^{T} C_p dT - T_o \int_{To}^{T} \frac{C_p}{T} dT + RT_o \ln\left(\frac{P}{P_o}\right) \tag{63}$$

The specific heat capacity (C_p) is calculated from the polynomial correlation of Barin [117] of type $C_p = a + bT + cT^2 + dT^3 + eT^4$. Values of the coefficients a, b, c, d, e for standard compounds are taken from the Aspen Plus library [56].

6.2.4.3. Total Exergy of a Stream

The total exergy of a stream is calculated as the sum of its chemical and physical exergy. Other contributions such as kinetic, potential or internal energy exergy are here neglected. Hence, for a stream consisting of a mixture of standard compounds, Eq.(64) can be applied, and the total exergy can be then rewritten as Eq.(65).

$$E_i = n_{tot} \cdot \left(\varepsilon_{ch,mix} + \sum_i x_i \cdot \varepsilon_{ph,i}\right) \tag{64}$$

$$E_i = n_{tot} \cdot \left(\sum_i x_i \cdot \varepsilon_{ch,i} + RT_o \sum_i x_i \cdot \ln(x_i) + \sum_i x_i \cdot \left(\int_{To}^{T} C_p dT - T_o \int_{To}^{T} \frac{C_p}{T} dT + RT_o \ln\left(\frac{P}{P_o}\right)\right)_i\right) \tag{65}$$

6.2.4.4. Exergetic Efficiency

Different definitions are being used for exergetic efficiency (Ψ_{ex}). In this chapter, rational efficiency defined by Kotas [115] is selected to compare the exergetic efficiency of all conversion routes and all biowastes. Hence, the exergetic efficiency of a process (Ψ_{ex}) is here calculated as the ratio of the desired exergy output (E_{output}) by the used exergy (E_{input}). In our 5 conversion routes, electricity and steam (heat) is co-produced and they are considered as outputs:

$$\Psi_{ex} = \frac{E_{output}}{E_{input}} = \frac{E_{biofuels} + W_{out} + E_{surplus\ steam}}{E_{biomass} + E_{utilities} + W_{in} + E^{Q}_{in}} \tag{66}$$

where $E_{biofuels}$, $E_{biomass}$, $E_{surplus\ steam}$, $E_{utilities}$ are the total exergy of biofuels, biomass, surplus steam and utilities respectively. As in energy balances, W represents the work being produced or added between the system and the environment. The total exergy of a heat flow (E^{Q}_{in}) can be calculated from the heat flows of a real process (Q_k) and the Carnot factor of a reversible process ($1 - T_o/T$), as follows:

$$E_k^{\ Q} = Q_k \cdot \left(1 - {T_o}/{T}\right) \tag{67}$$

Table 6.6 shows the exergetic efficiency of the 5 biofuels chains using 5 different biowastes streams, where the exergetic efficiency is calculated from Eq.(66). Results will be later compared with the overall energy efficiency presented in previous sections (see section 6.2.5).

Table 6.6. Comparison of overall exergetic efficiency (Ψ_{ex}) for different biofuels and biowastes

Biofuel	Parameter	Stream A	Stream B	Stream C	Stream D	Stream E
SNG	Ψ_{ex}	69%	68%	71%	66%	67%
Methanol	Ψ_{ex}	58%	57%	59%	56%	58%
Fischer- Tropsch	Ψ_{ex}	58%	57%	62%	53%	55%
Hydrogen	Ψ_{ex}	55%	54%	57%	54%	54%
Heat and Electricity	Ψ_{ex}	43%	42%	45%	42%	40%

As observed, SNG production is the most efficient process, whereas heat and electricity generation achieved lower rates. Analogous to previous calculations, dry streams (A and C) are again preferred. However, in this case, the driest stream (A) is not the best option. One possible explanation could be that stream (A) requires more work input, heat and steam, and although a higher amount of biofuel is produced, this higher production does not compensate the input demands. The methanol processes is less efficient than SNG. In fact, it produces more biofuels but it also requires more energy to run the process.

On the other hand, Fischer-Tropsch and hydrogen chains achieve similar exergetic efficiencies. However, the main difference is that hydrogen plant generates a lower amount of H_2 biofuel but more electricity from unconverted gases and heat removal. In fact, a surplus of electricity is produced and it could be eventually sent to the grid. Moreover, energy density of hydrogen (MJ/kg) is around 3-fold higher than the corresponding for Fischer-Tropsch product. Conversely, Fischer-Tropsch process produces a higher amount of biofuels but the electricity produced cannot cover the demand of the process itself. Results are compared with values found in literature in Table 6.7, although in many cases, the processes have different operation units and biomass composition, which, in turn, affect the overall exergetic efficiency.

Table 6.7. Comparison of Ψ_{ex} evaluated for the case of wood wastes (stream A) with values found in literature

Analysis	Symbol	SNG	Methanol	Fischer-Tropsch	Hydrogen	Heat and Electricity
Our case (stream A)	Ψ_{ex}	69%	58%	58%	55%	43%
Literature values (wood)	Ψ_{ex}	69%[(a)] [118]	56%[(b)] [119]	36 % [119]	66% [119] 45-51%[(c)] [120] 63-66%[(d)][120]	33%[(e)] [121]

(a) Exergetic efficiency for steam-blown direct gasification.
(b) Exergetic efficiency for sludge gasification.
(c) Without heat recovery
(d) With heat recovery
(e) With internal combustion engine combined cycle (ICE-CC)

Exergetic efficiency based only on the chemical exergetic content of the biowastes and the biofuels ($\Psi_{\varepsilon ch}$) is also applied to compare the corresponding results with the LHV efficiency (η_{LHV}) obtained from Eq.(53), and the corresponding values are discussed in section 6.2.5. The chemical exergetic efficiency is calculated according to the following relation:

$$\Psi_{\varepsilon,ch} = \frac{m_{biofuel} \cdot \varepsilon_{ch,biofuel}}{m_{biowaste} \cdot \varepsilon_{ch,biowaste}} = \frac{m_{biofuel} \cdot \varepsilon_{ch,biofuel}}{m_{biowaste} \cdot \beta \cdot LHV_{biowaste}} \tag{68}$$

6.2.5. Comparison of Different Efficiency Analysis

Table 6.8. Comparison of HHV and LHV ratios (Eqs.(52-53)) with chemical exergetic efficiency calculation (Eq.(68))

Biofuel	Parameter	Stream A	Stream B	Stream C	Stream D	Stream E
SNG	η_{HHV} (η_{LHV})	71 (69)%	69 (67)%	70 (67) %	68 (66) %	69 (66%)
Methanol	η_{HHV} (η_{LHV})	64 (60)%	57 (53)%	57 (53) %	49 (46) %	63 (59%)
Fischer- Tropsch	η_{HHV} (η_{LHV})	68 (67)%	68 (67)%	70 (69)%	66 (65)%	63 (62)%
Hydrogen	η_{HHV} (η_{LHV})	73 (66)%	73 (66)%	75 (67) %	73 (66) %	72 (65) %
Heat and Electricity	η_{HHV} (η_{LHV})	58 %	57 %	59 %	55 %	55 %
SNG	$\Psi_{\varepsilon,ch}$	57 %	48 %	52 %	34 %	46 %
Methanol	$\Psi_{\varepsilon,ch}$	54 %	47 %	50 %	40 %	52 %
Fischer- Tropsch	$\Psi_{\varepsilon,ch}$	58 %	59 %	64 %	56 %	57 %
Hydrogen	$\Psi_{\varepsilon,ch}$	51 %	51 %	55 %	49 %	50 %
Heat and Electricity	$\Psi_{\varepsilon,ch}$	62 %	61 %	63 %	60 %	59 %

Table 6.9. Comparison of traditional energy efficiency calculation (Eq.(54-55)) with exergetic efficiency calculation (Eq.(66))

Biofuel	Parameter	Stream A	Stream B	Stream C	Stream D	Stream E
SNG	$\Psi_{HHV}(\Psi_{LHV})$	72 (69)%	70 (68)%	71 (68)%	65 (63)%	69 (67)%
Methanol	$\Psi_{HHV}(\Psi_{LHV})$	69 (67)%	64 (62)%	64 (62)%	61 (60)%	64 (62)%
Fischer- Tropsch	$\Psi_{HHV}(\Psi_{LHV})$	67 (66)%	67 (66)%	69 (68)%	65 (64)%	64 (63)%
Hydrogen	$\Psi_{HHV}(\Psi_{LHV})$	66 (61)%	66 (61)%	67 (61)%	66 (61)%	65 (60)%
Heat and Electricity	$\Psi_{HHV}(\Psi_{LHV})$	46 (48)%	46 (48)%	47 (49)%	43 (46)%	44 (47)%
SNG	Ψ_{ex}	69%	68%	71%	66%	67%
Methanol	Ψ_{ex}	58%	57%	59%	56%	58%
Fischer- Tropsch	Ψ_{ex}	58%	57%	62%	53%	55%
Hydrogen	Ψ_{ex}	55%	54%	57%	54%	54%
Heat and Electricity	Ψ_{ex}	43%	42%	45%	42%	41%

As observed in Tables 6.8 and 6.9, exergetic efficiencies are lower than the corresponding energy efficiencies, as exergy takes into account degradation of energy quality.

6.2.5.1. Exergy Losses of a Process (Irreversibilities)

Unlike ideal processes, exergy is consumed during real processes and the corresponding exergy consumption rate is proportional to the entropy created due to process irreversibilities. Identifying irreversibilities within a process or system is compulsory when intending to optimize its thermodynamic performance. For that purpose, the Eq.(69) has been applied in each part of the process, ranging from biowastes pre-treatment to final upgrading of the biofuels:

$$I = \sum_{in} E_i - \sum_{out} E_j + E_{in}^{\ Q} - E_{out}^{\ Q} + W_{in} - W_{out} \tag{69}$$

where I (in MW) stands for irreversibilities (exergy losses), and E_i, E_j are the exergy associated with the compounds (i) and (j) entering and leaving streams respectively. Results from this analysis are presented in Figures 6.1 - 6.5. As observed, the gasifier is the main contributor to the exergy losses, except for the heat and electricity route where the combined cycle is less efficient. Hence, further effort must be devoted to firstly improve the performance of the gasifier by changing operational parameters such as pressure or temperature. Some authors have already done some studies about the influence of some operational parameters of the gasifier on the overall exergetic efficiency of the plant.

For instance, Prins *et al.* found that, for Fischer-Tropsch fuels synthesis, an increase of the gasification temperature lead to a decrease on the gasifier and overall exergetic efficiency, whereas an increase of the drying extend benefit the exergetic efficiency of both the gasifier and the plant [91]. Jurascik *et al*. found the same trend for a wood-to-SNG routes, and they also determined that increasing gasification pressure have a good influence on the overall exergetic efficiency [118, 122].

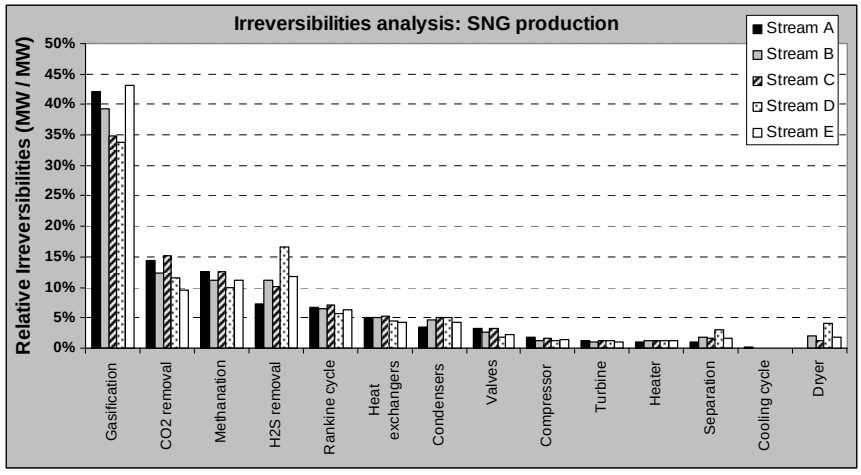


Figure 6.1. Irreversibilities (exergy losses) of the biowastes-to-SNG conversion routes.

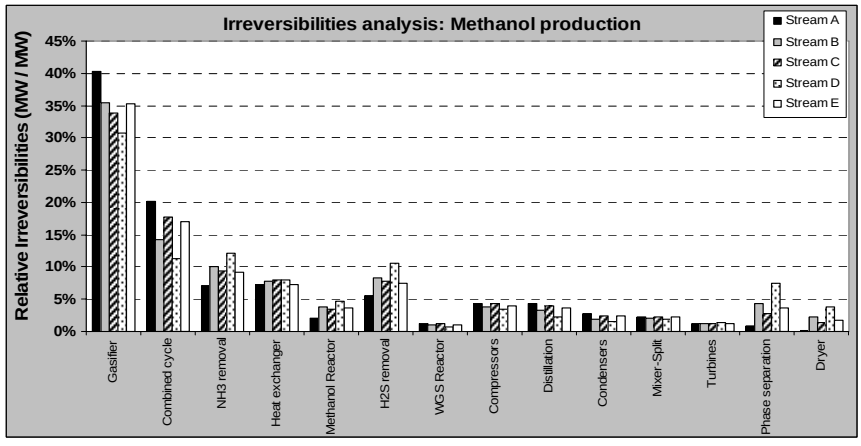


Figure 6.2. Irreversibilities (exergy losses) of the biowastes-to-methanol conversion routes.

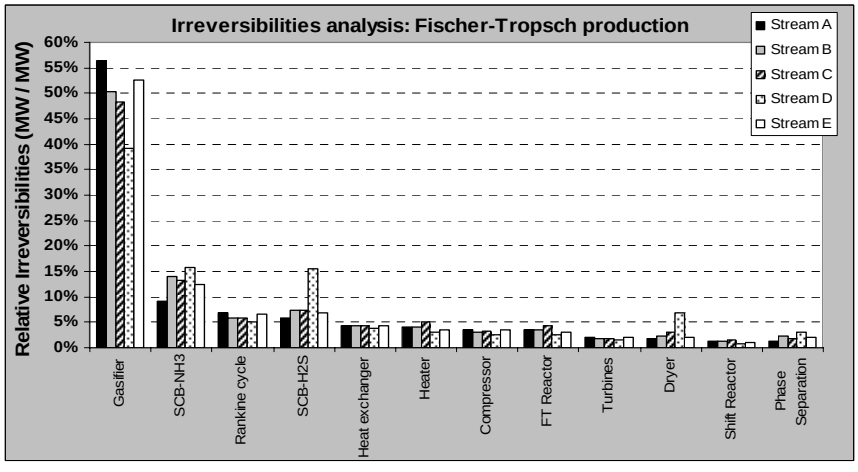


Figure 6.3. Irreversibilities (exergy losses) of the biowastes-to-Fischer Tropsch conversion routes.

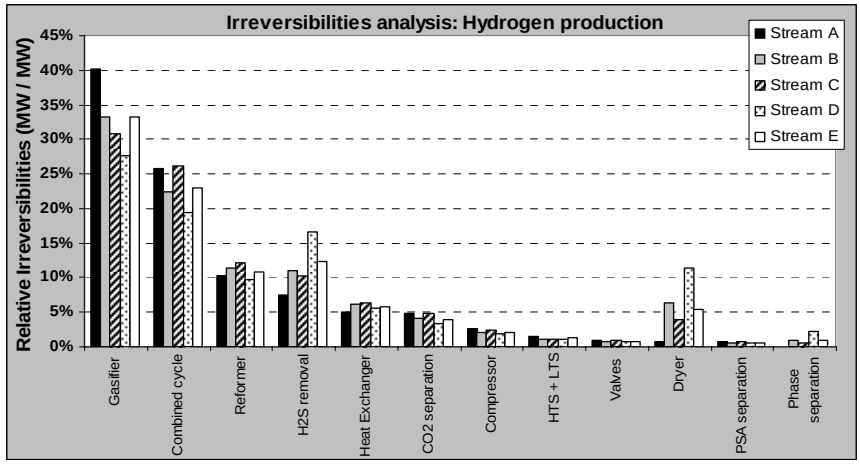


Figure 6.4. Irreversibilities (exergy losses) of the biowastes-to-hydrogen conversion routes.

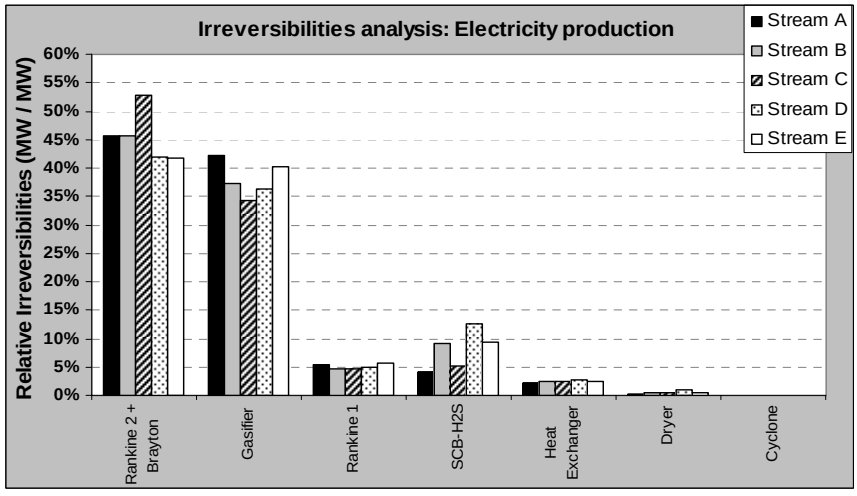


Figure 6.5. Irreversibilities (exergy losses) of the biowastes-to-electricity conversion routes.

Electricity co-production in biofuel routes also represents an important share of exergy losses. In fact, irreversibilities of these cycles can be reduced by operating at different pressures or temperatures and by improving heat integration. Cleaning stages (e.g., H_2S, NH_3 and CO_2 removal) are also an important source of irreversibilities and different technologies could be studied in order to decrease their share.

7. SUSTAINABILITY EVALUATION

As mentioned in section 1, many definitions exist about sustainability, but in a general, sustainability is defined as "*the capacity to maintain a certain process or state indefinitely*". Applied to the human community, sustainability has been expressed as "*meeting the needs of the present without compromising the ability of future generations to meet their own needs*" (U.S. Environmental Protection Agency). However, from a scientific point of view,

sustainability is rather difficult to evaluate and/or quantify. In fact, there are basically two major "barriers" for sustainability evaluation. Firstly, there is not concise standard definition approved by the scientific community yet, and many divergent definitions and criteria can be found in literature. Moreover, factors affecting the sustainability of any process or system have different units of measurement and, hence, they cannot be integrated into one value unless conversion factors are available.

In our analysis, sustainability is defined as a combination of 3 key factors, i.e., efficiency, economy and socio-environment impact, and a comparison has been made with other criteria and definitions found in literature. In general, most of the approaches can be accommodated into our definition, and an example is given in Figure 7.1. As observed, the 6 *"Cramer"* sustainability criteria for biomass conversion can be gathered into our 3 key factors. These 6 criteria has been set by the current Dutch minister of Housing, Spatial Planning and the Environment, Jacqueline Cramer [123].

In this section, the economic and environmental impact of the 5 biowastes-to-biofuels routes are discussed, in order to complete the previous presented exergetic efficiency concept (see section 6).

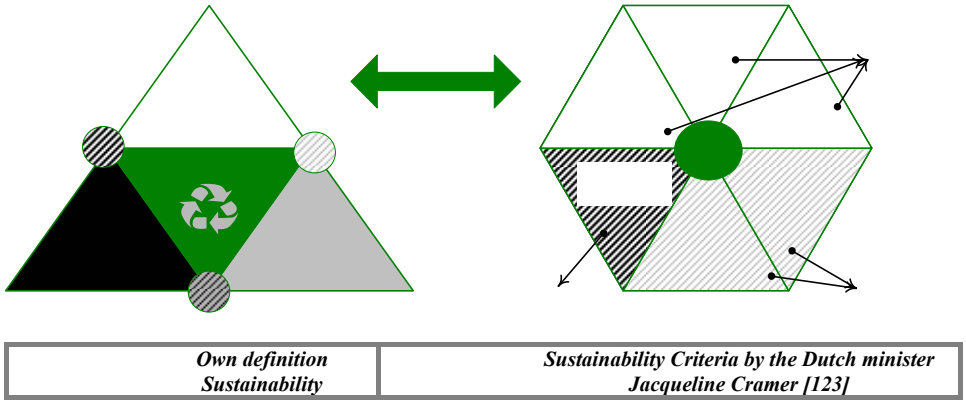


Figure 7.1. Analogies between our definition for sustainability and the sustainability criteria set by the Dutch Minister of Housing, Spatial Planning and the Environment, Jacqueline Cramer.

7.1. Environmental Impact

In the previous section 6, several thermodynamic analyses, especially the exergetic evaluation, are used to improve processes performance. However, those analyses do not make any distinction between fossil fuels and biofuels toxicity and/or environmental impact. *Life Cycle Analysis* (LCA) is a well-known methodology that can be used for that purpose. According to the ISO-14040, LCA is defined as *''the compilation and evaluation of the inputs, outputs and potential environmental impacts of a product throughout its life cycle.'',* and it consists of 4 main procedures: (1) Goal and scope definition, (2) Inventory analysis, (3) Impact assessment, (4) Interpretation and action.

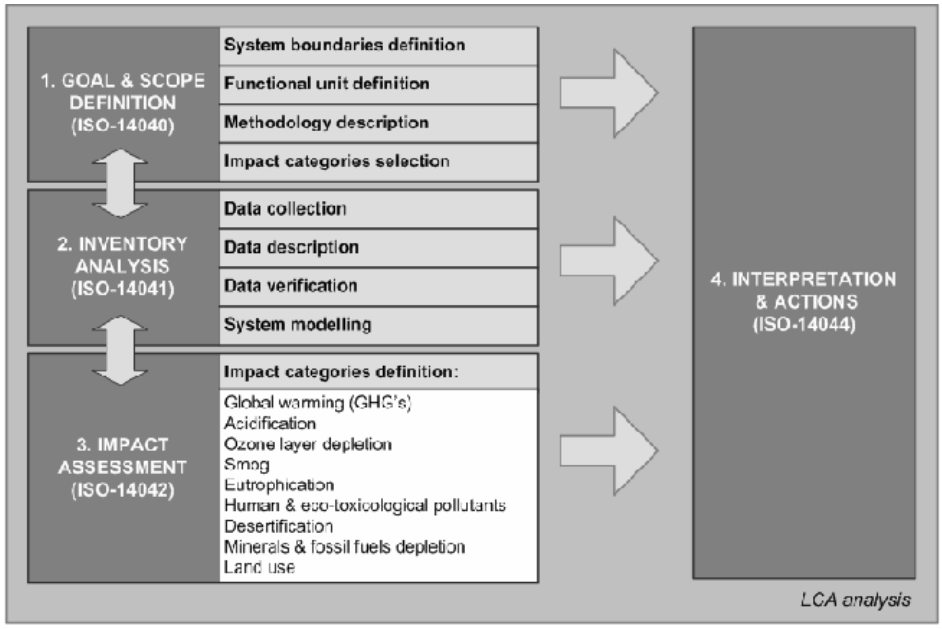


Figure 7.2. Schematic representation of a LCA analysis.

During the preparation of an LCA, some environmental parameters need to be defined in order to quantify the impact of a process or product. These "impact categories" can include: acidification, GHG emissions, eutrophication, ozone depletion, land use and many more. Figure 7.2 gives a schematical representation of the LCA methodology and its main stages. LCA analysis has not been applied yet in our simulations but values found in literature are presented and discussed in this section for the 5 discussed conversion routes, i.e., SNG, methanol, Fischer-Tropsch fuels, hydrogen and electricity. Unlike first generation biofuels, second generation biofuels make use of the whole plant, which directly increases the area-specific yield of biofuels. Hence, they should perform better in terms of GHG's emissions but, in general, no single technology is advantageous over another [9, 111, 124].

In fact, when taking into account the whole production chain, the GHG's emissions reduction are still minor. LCA analysis can reveal the major impacts of each step in order to improve the process from the environmental point of view.

7.1.1. Biomass-to-SNG Evaluation

Experts of the Paul Sherrer Institute [125] have evaluated and compared the ecological impacts of using SNG vs. fossil fuels in heating and passenger cars systems. For the life cycle impact assessment (LCIA), two different methodologies have been used: the Eco-indicator'99 [126] (EI'99) with 3 different perspectives (i.e., Hierarchist, Egalitarian and Individualist) and the Eco-scarcity [127]. The system boundaries covered all processes of biomass growing, collection and conversion to one energy service (i.e., 1 MJ of useful heat or passenger-kilometers). Results from their studies show that, when the evaluation method strongly weighted the use of fossil fuels (i.e., EI'99 Hierarchist and Egalitarian perspectives), the SNG heating system qualified better than the gas or oil heating systems. However, when the use of fossil fuels was less weighted (i.e., EI'99 Individualist and Eco-scarcity perspective), the natural gas heating system attained the lowest impact score due to its higher efficiency and

relatively low emissions, whereas the SNG system involved higher NO_x and particulates emissions. In any case, the oil heating system obtained the worst impact score. Moreover, the relative score of the SNG heating system could be still improved if polygeneration were considered, as this would increase the overall efficiency of the SNG plant as well as reduce the need of grid electricity.

**On the other hand, the SNG car system had the lowest impact score compared with the conventional fossil fuelled cars when using the EI'99 Hierarchist and Egalitarian perspectives. However, when neglecting the use of fossil fuel resources and boosting the use of metal resources, the SNG system was evaluated nearly as ecologically efficient as the natural gas. Moreover, all the methods suggested that using SNG for fuelling passengers cars is environmentally preferred that burning SNG for heating systems.*

7.1.2. Biomass-to-Methanol Evaluation

Pehnt et al [128] have conducted an LCA to compare the environmental impact of using fossil fuels and methanol in indirect combustion engines (ICE) and fuels cells vehicles (FCV). Methanol is produced from either natural gas reforming or wood gasification. For their study, 6 impact categories have been investigated: use of non-renewable energy, eutrophication, global warming, summer smog, acidification and carcinogenic emissions. Results are gathered in Figure 7.3 in order to obtain a complete picture of the environmental performance of the different power train and fuel options. As observed, methanol from wood-gasification is the best alternative when comparing the impact categories of non-renewable fuel consumption (nr.1) and global warming (nr.3). Although methanol fuel cells (FCV) are around 2-3 more efficient than traditional vehicles (ICE) [13], more energy is required to built the fuel cell cars and hence, this option turn out to have a greater global warming impact.

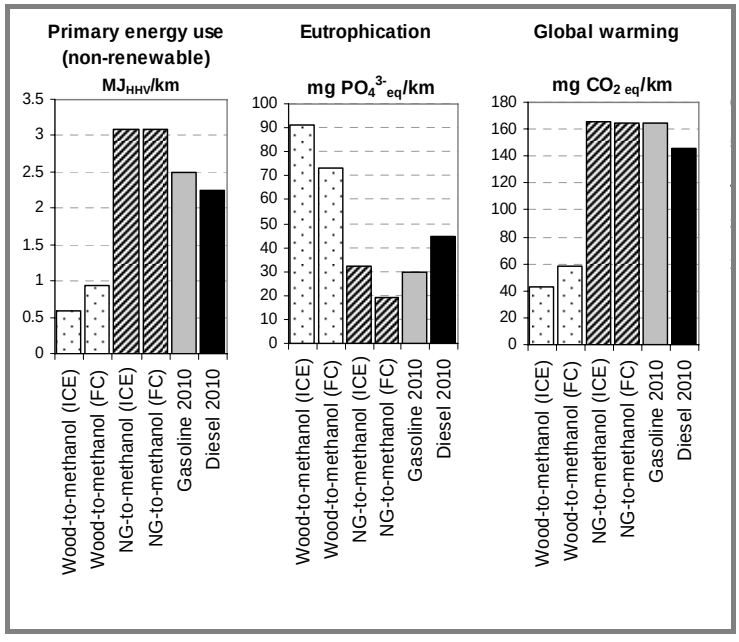


Figure 7.3. Continued on next page.

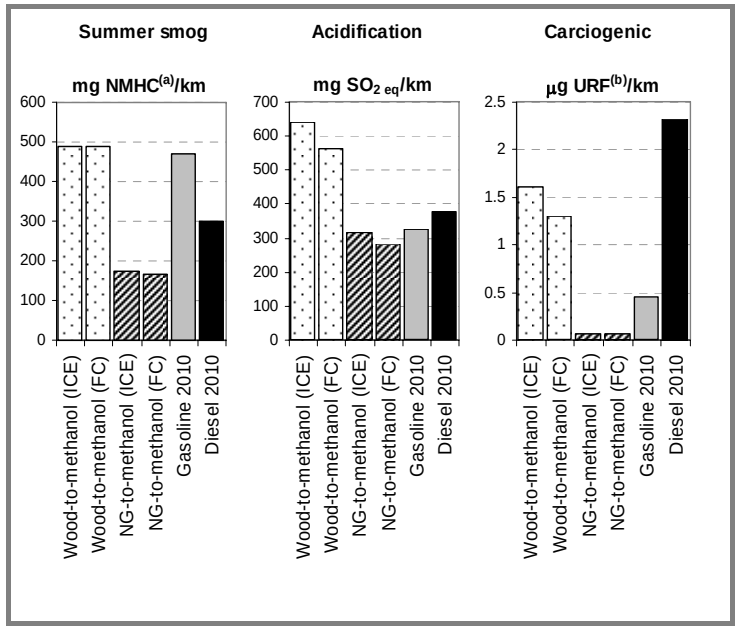


Figure 7.3. Environmental impacts comparison for different power trains and fuel options. Results are compared on the basis of mobile application (km per vehicle) [128].

Wood-to-methanol for either fuel cell (FCV) and combustion engine vehicles (ICE) are less advantageous to the rest of impact categories, being even the worst scenario for eutrophication, summer smog and acidification categories due to combustion of purge gas. Most of the eutrophication emissions for the wood-to-methanol route comes form the feedstock itself, whereas for the case of fossil diesel the highest contribution is due to car manufacturing. Carcinogenic emissions originate from the off-road equipment for wood collection and transshipment. For the case of woody wastes, this impact will be then less important.

7.1.3.Biomass-to-Fischer Tropsch Fuels Evaluation

PE-Europe GmbH [129], on behalf of Volkswagen AG and Daimer Chrysler AG, have conducted a LCA analysis for the production and consumption of SunDiesel, i.e., a synthetic diesel produced by Fischer-Tropsch synthesis using the Choren Process [10, 90].

The study takes into account the complete lifecycle of the SunDiesel from the collection of raw materials until its final use in a combustion engine, and the results were compared with a conventional diesel system. In the course of the study, 4 impact categories have been investigated (i.e., global warming potential, acidification, eutrophication and winter smog effect emissions) under 3 different scenarios:

- *"Self-Sufficiency Basis Scenario" (Case A):* it accounts for the existing status of the Choren Process at the Freiberg plant in Germany. In this scenario, wood is used to co-produce electricity, oxygen and hydrogen required for the process, so as hardly any external energy supply is needed.
- *"Future Scenario" (Case B):* it envisages the possibility of supplying energy, oxygen and hydrogen from renewable sources * instead of consuming more wood. Hence,

the mass conversion yield to SunDiesel will be higher as more wood could be dedicated to the Fischer-Tropsch unit.

- *"Partial Self-Sufficient Scenario" (Case C):* it considers the option of producing hydrogen from a WGS reaction, whereas oxygen and electricity would be supplied externally.

Results from these 3 different scenarios are represented in Figure 7.4. As observed, the case A is the most environmentally friendly situation regarding the global warming and summer smog categories, whereas the case C is the better option for the eutrophication and acidification categories.

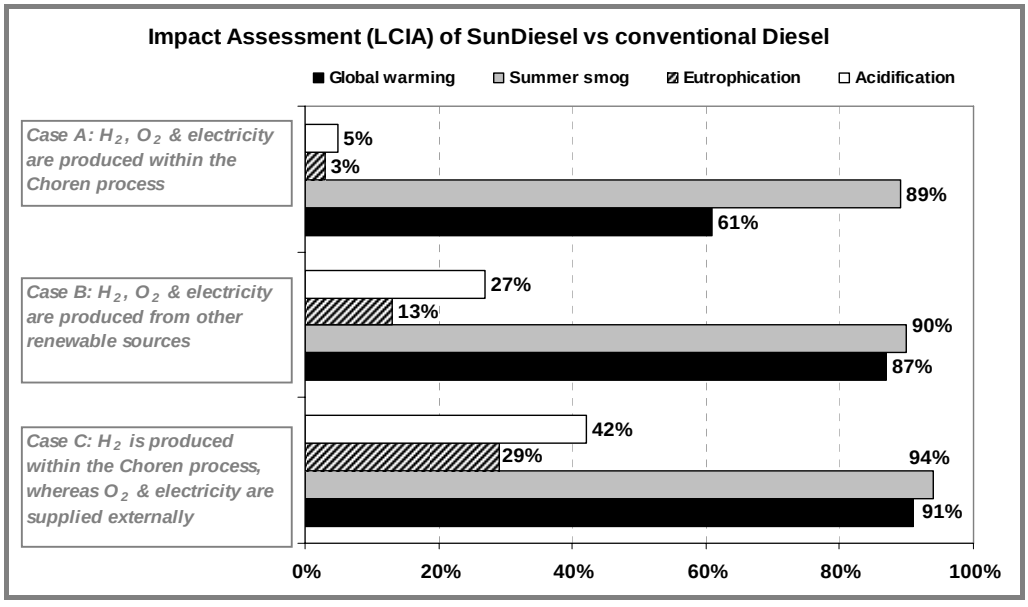


Figure 7.4. Potential reduction of environmental impact under 3 different scenarios and in comparison with conventional diesel. Data is taken from Baitz *et al*. [129]. Values indicate the reduction of emissions compared to a car fueled with fossil diesel.

7.1.4. Biomass-to-Hydrogen Evaluation

Koroneos et al [102] studied the technical and environmental performance of two different biomass-to-H_2 systems by means of a LCA analysis and the Ecoinvent'95 methodology for the LCIA . The first system is similar to our hydrogen chain simulation and mainly consists of biomass gasification, steam reforming, high (HTS) and low (LTS) temperature shift reactions, and pressure-swing-absorption (PSA) separation that recovers hydrogen with a purity of 99%. In the second process, biomass gasification is followed by electricity generation in a combined cycle, and the electricity generated is used to obtain hydrogen via electrolysis. Finally, the hydrogen is liquefied to –253^{o}C by a combination of isothermal compression and adiabatic expansion, whereby the gas is cooled due to the Joule Thomson effect. The LCA analysis covered the stages of materials acquisition, manufacturing, use/reuse/maintenance and recycling/waste management. According to their results the first gasification-PSA route achieved higher energy efficiency (1 TJ H_2/2.4 TJ

energy input) than the gasification-electrolysis route (1 TJ H_2/4.2 TJ energy input). Conversely, the gasification-electrolysis route has a better environmental performance as it has an overall environmental impact score of 263.4 compared to 123.03 for the gasification-PSA route.

Same authors [130] compared the environmental impact of using hydrogen from renewable and fossil fuels sources vs. kerosene in aviation. For that purpose, they evaluate 4 impact categories: GHG's emissions, acidification, eutrophication and winter smog effect emissions. The study concluded by stating that the production of hydrogen from renewable sources has a considerably low environmental impact, although the authors questioned the reliability of its continuous production. Among all the aviation fuel systems, the kerosene cycle resulted in the less environmental friendly fuel in most of the impact categories. Conversely, hydrogen production from wind and hydropower energy become the less polluting systems even for long distance travels. Biomass and solar thermal energy also lead to very low emissions, whereas photovoltaic systems represented the worst case within the renewable alternatives.

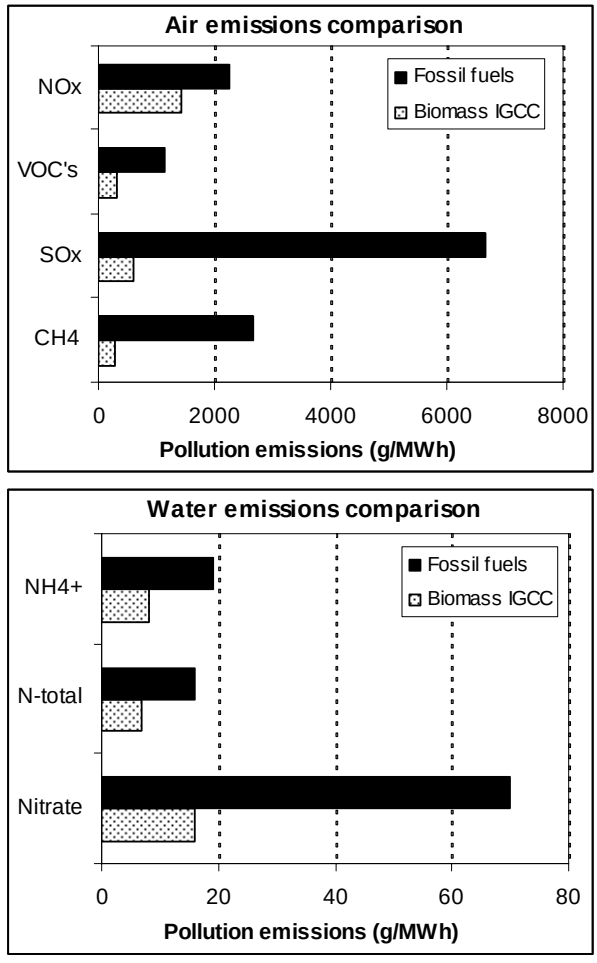


Figure 7.5. Comparison of air and water emissions (g/MWh) for both systems: IGCC fuelled with biomass and a conventional power generation system fuelled with 50% coal and 50% oil.

7.1.5. Biomass-to-Electricity Evaluation

Rafaschieri et al [131] applied a traditional LCA analysis for two different electricity generation technologies, i.e., an IGCC system fuelled with energy crops and a conventional power generation system fired with 50% of coal and 50% of oil. In this study, they also compared the environmental impact of using different operational conditions in the gasifier unit as well as air and oxygen as gasifying agents. Similar to the work of Koroneos et al [102], Ecoinvent'95 methodology was adopted for the LCIA evaluation with 9 selected impact categories: GHG's emissions, acidification, eutrophication, summer smog, ozone layer depletion, energy consumption, carcinogens, pesticides, and heavy metals deposition. According to their results, the conventional fossil fuel powered system has a larger impact in all categories except for pesticides usage, ozone depletion and eutrophication emissions (PO_2eq/MWh). In particular, CO_2 emissions are reduced from 930kg/MWh to 110 kg/MWh when using the biomass-based IGCC process (i.e., a reduction ratio by 8.5). As shown in Figure 7.5, other air and water emissions are also lowered.

Same authors also found that the use of air as oxidizing agent causes about 2 to 7 less environmental effects than when gasifying with pure oxygen. However, about 99% of this larger impact comes from the electricity consumed to produce oxygen. Alternatively, oxygen production within the production plant is only economic feasible for plant sizes above 100 MW_e [131].

7.2. Economic Analysis

Some selected results on economic analysis are presented in Table 7.1 in order to give a general overview about biofuels production costs. In Table 7.1, production costs of the 5 discussed biofuels (i.e., SNG, methanol, Fischer-Tropsch fuels, hydrogen and electricity) are compared with the corresponding costs of biochemical treatments (i.e., biogas, bioethanol, biodiesel and bio-hydrogen), whereas the last column stands for the current prices of fossil fuels. However, it should be noticed that these analyses are not performed on the same basis and, hence, side-by-side comparison of the different biofuels is rather difficult and inaccurate. In fact, these analyses make use of different plant sizes, different feedstocks costs, diverse economic parameters as well as different methodologies to calculate capital and operating costs.

In general, biofuels production costs are still not competitive with current fossil fuels prices, but this tendency could change in the future when more restrictive emissions limits and taxes will be agreed. Moreover, fossil fuel prices are projected to increase considerably in the coming years due to reservoirs depletion and market speculation. Although biofuels costs are directly affected by production scales, they can be found in the range of 4.5 €/GJ (SNG) to 30 €/GJ (Fischer-Tropsch). In particular, Fischer-Tropsch fuels costs can be drastically decreased from 30 to 15 €/GJ when considering large production scales of about 8,500 MWth.

Table 7.1. Production costs comparison of biofuels and prices of fossil fuels

Method ➡ Biofuel ⬇	Thermochemical conversion (production costs)	Biochemical conversion (production costs)	Fossil fuels (prices)
Methane	Gasification (SNG): [(h)] 5.1-11.6€$_{2020}$/GJ [20] [(i)] 4.5-11.1€$_{2020}$/GJ [20]	Anaerobic digestion (biogas): 6-10U$$_{2008}$/GJ	Gas (without taxes) [132]: Europe-27: 7.12€$_{2007}$/GJ
Ethanol	Gasification (ethanol): [(g)] 12$$_{2012}$/GJ [133]	Fermentation (bioethanol): [(b)] 5.2U$$_{2001}$/GJ [134] [(d)] 22-13U$$_{2004}$/GJ [135]	-
Methanol	Gasification (methanol): [(a)] 14–17U$$_{2001}$/GJ [14, 101] [(b)] 5.3U$$_{2001}$/GJ [134] [(c)] 9–12U$$_{2001}$/GJ [13] [(n)] 9.6–15.4U$$_{1991}$/GJ [136]	-	Methanol (fob prices) [137]: West Europe: 336 €$_{2007}$/ton (~14.8 €$_{2007}$/GJ)
Fischer-Tropsch fuels	Gasification (F-T fuels): [(e)] 16€$_{2002}$/GJ [17, 18] [(f)] 9-11.5€$_{2017}$/GJ [17, 18] [(j)] 15-30€$_{2006}$/GJ [19]	Biodiesel (transesterification): 9-21 U$$_{projected}$/GJ [138] 15.9 U$$_{2005}$/GJ [139]	Diesel (without taxes) [132]: Netherlands: 605.31€$_{2007}$/m^3 (~16.6 €$_{2007}$/GJ)
Hydrogen	Gasification (hydrogen): [(a)] 10–14U$$_{2001}$/GJ [14, 101] [(b)] 5.2U$$_{2001}$/GJ [134] [(c)] 8–11U$$_{2001}$/GJ [13] [(M)] 14–21U$$_{2000}$/GJ [140]	Biohydrogen (fermentation): 30 €$_{2008}$/GJ [141]	From natural gas (global): 5-8U$$_{2003}$/GJ but market prices are ~ 45$/GJ [142]
Electricity	IGCC (heat and electricity): [(k)] 6.6-8.2 ¢$$_{1996}$/GJ [63] [(l)] 5.4-11.3 ¢$$_{1990}$/GJ [63]	From biogas: 7.2¢€$_{2003}$/kWh [143] 14.5-15.1¢€$_{2008}$/kWh [144]	Prices for industry [132]: Europe-27: 7.08¢€$_{2007}$/kWh Netherlands: 6.61¢€$_{2007}$/kWh

[(a)] assuming that biomass would be delivered at 2.3 US$/GJ, and production scales up to 400 MW_{th}.

[(b)] assuming biomass from dedicated eucalyptus plantations, and production scales up to 530 MW_{th}.

[(c)] assuming that biomass would be delivered at 2.0 US$/GJ, and production scales up to 400 MW_{th}.

[(d)] assuming biomass from lignocellulosic materials and delivered at 2-3 US$/GJ, and production scales up to 400 MW_{th}.

[(e)] assuming conventional technologies, biomass delivered at 3 €/GJ, and production scales up to 400 MW_{th}.

[(f)] assuming advanced technologies in 15 years, biomass delivered at 2-3 €/GJ, and larger production scales up to 2000 MW_{th}.

[(g)] study based on the possibility of producing lignocellulosic bioethanol via gasification at a production cost competitive with traditional corn-ethanol, i.e., 1.07U$/gallon or 12U$/GJ.

[(h,i)] assuming that biomass would be delivered at 2.5-3.6 €/GJ, and production scales up to 100 MW_{th}; (h) refers to the case of oxygen-blown pressurized gasifier whereas (i) refers to the case of indirect Battelle gasification

[(j)] assuming that biomass would be delivered at 4.0 €/GJ. The production costs are directly related to plant scales, i.e., 30 €/GJ for 8,500 MW_{th} or 15 €/GJ for 50 MW_{th}.

[(j)] assuming that biomass would be delivered at 42U$/tn, and production scales in the range of 56-105MW_{th}.

[(l)] assuming that biomass would be delivered at 17-42U$/tn, and production scales in the range of 50-105MW_{th}.

[(m)] assuming that biomass would be delivered at 2.7 US$/GJ, and a plant size of 23-114 H_2 ton/day.

[(n)] assuming biomass delivered at 2 U$/GJ, and production scales in the range of 706-1,004 biofuel ton/day.

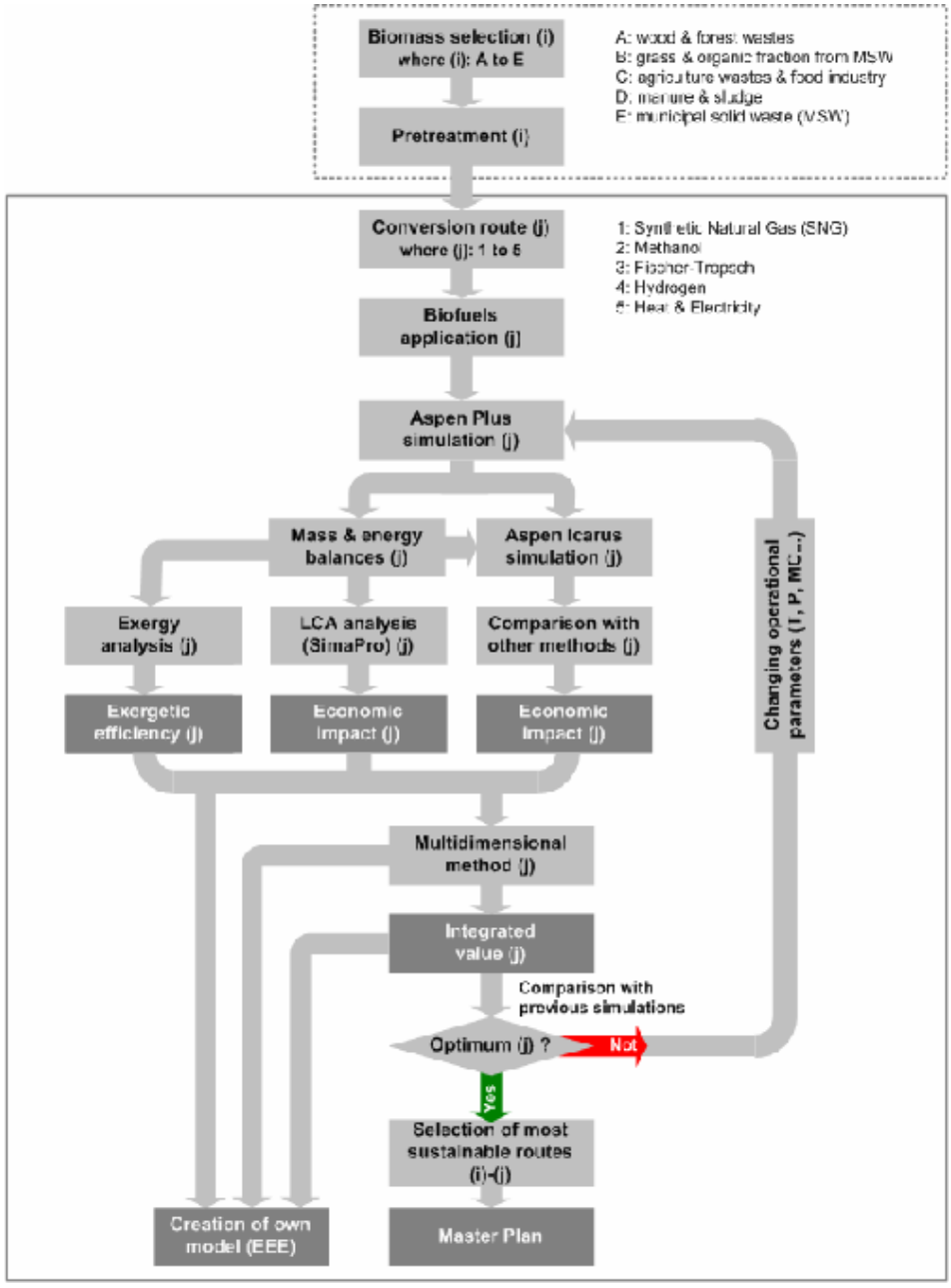


Figure 7.6. Overview of the stages required to create an own accounting model and a Master Plan for Friesland. The own model (named EEE) will be based on already existing multidimensional methods such as EEA.

7.3. Unidimensional and Multidimensional Accounting Methods

As aforementioned, sustainability of a process is rather difficult to evaluate and quantify as many factors are involved and they are also given in different units. For instance, environmental impact is measured in ppm (or gCO_2eq/kg biofuel for the case of global

warming evaluation), whereas production costs are given in €/$GJ_{biofuel}$, and efficiency is calculated as the ratio of energy output divided by the energy input (i.e., $MW_{outputs}/MW_{inputs}$). Hence, conversion factors are required if we intend to give one unique parameter in order to be able to communicate with scientists, legislators and economists at once.

Hence, using independent unidimensional methods such as exergy, LCA and Life Cycle Cost (LCC) does not seem to be the ultimate alternative. Multidimensional accounting methods such as Cumulative Exergy (CExC) and Exergetic Life Cycle Analysis (ELCA) take into account the exergy consumption of the whole production chain, analogous to the LCA for the environmental impact assessment.

Recently, Extended Exergy Accounting (EEA) and Thermo-Economics (TE), have been proposed as an extension of the unidimensional methods to interlink the technical, economic, and socio-environmental issues. Table 7.2 summarizes some of these approaches.

In future, the EEA method developed by Sciubba et al will be used as a reference to built an own proper model that would integrate the 3 key parameters, i.e., efficiency, economic and environmental impact. The province of Friesland will be used as a case study to implement our model and finally elaborate a Master Plan that could be used for strategic decisions of the and/or for regional policy making. Figure 7.6 schematically presents the designed pathway for elaborating the own model and the final Master Plan.

Table 7.2. Comparison of unidimensional and multidimensional accounting methods

Accounting method	Methodology	Exergetic efficiency (MW_{output}/MW_{inputs})	Environmental impact (ppm)	Economic analysis (€/$GJ_{biofuel}$)
Uni-dimensional	Traditional energy efficiency[(a)]	✓		
	Exergy analysis[(b)]	✓		
	LCA (Life Cycle Analysis)		✓	
	LCC (Life Cycle Cost)			✓
Multi-dimensional	TE (Thermo-Economics)	✓		✓
	ELCA (Exergetic Life Cycle Analysis)	✓	✓	
	CExC (Cumulative exergy)	✓	✓	
	EEA (Extended Exergy Accounting)	✓	✓	✓

[(a)] Method less accurate to evaluate the efficiency of a process as it is only based on the 1st law of Thermodynamics.

[(b)] Method more accurate to evaluate the efficiency of a process as it is based on the 1st and 2nd law of Thermodynamics.

CONCLUSIONS

First generation biofuels (e.g., bioethanol and biodiesel) are already well-established at commercial scale worldwide, being Brazil the leading country on bioethanol production. However, one of the main drawbacks of those processes is that they consume sugars and vegetable oils from dedicated energy crops, which triggers land competition for food production. Moreover, some experts have questioned the environmental impact reduction of

first generation biofuels in comparison with fossil fuels. Second generation biofuels are now under development as there are expected to achieve higher efficiencies from non-edible feedstocks such as lignocellulosic materials and biowastes. Using thermochemical technologies such as biomass gasification could lead to higher efficiencies and larger scales. This chapter presents the simulation and efficiency evaluation of different second generation biofuels (i.e., SNG, methanol, Fischer-Tropsch fuels, hydrogen as well as heat-electricity) obtained via gasification of five biowastes streams from the Dutch province of Friesland. Efficiency evaluation has been carried out by means of different approaches, including mass conversion yield, traditional energy efficiency and exergetic efficiency.

Results showed that methanol (followed by SNG and Fischer-Tropsch) is the best option when considering mass conversion as the key parameter, irrespectively of the biowaste stream used. Mass conversion yields of methanol production are the highest, i.e., 16-48%, whereas H_2 production from wood only reached 9-11% of mass conversion. However, mass conversion yield is not an accurate parameter to select the most convenient biowaste-to-biofuels route as it only gives a rough estimate of the amount of biowaste that is converted to biofuel. The second analysis presented in this chapter refers to the traditional energy efficiency concept which is based on the 1st Law of thermodynamic.

In this case, SNG production is the most efficient process (i.e., 65-72%), whereas methanol, Fischer-Tropsch and hydrogen production achieved similar efficiencies (i.e., 61-69%), as shown in Table 6.9. As expected, electricity production is the less efficient process (i.e., 43-47%). However, in our analysis, we have not included the inefficiencies of biofuels application and, hence, it could happen that direct electricity production may turn out to be the preferred alternative. Traditional energy efficiency analysis is also compared with more recent exergetic efficiency analysis, which is considered to be more accurate as it also takes into account the energy quality degradation (i.e., the 2nd Law of thermodynamic). Results show that exergetic efficiencies are lower than energy efficiencies, but SNG is still the preferred process. The values obtained are 67-71% for SNG, and around 53-59% for the rest of biofuels, i.e., methanol, Fischer-Tropsch and hydrogen, as shown in Table 6.9. Heat and electricity production again achieved the lowest exergetic efficiency, i.e., 41-45%. An exergy analysis reveals that the gasifier is always the unit with higher exergy losses (i.e. 35 to 55%). Single and combined cycles for electricity generation, as well as cleaning stages have also an important share of exergy losses. Further optimization based on better heat integration and modification of operational parameters such as pressure and temperature (especially in the gasification unit) could enhance the overall efficiency of the processes.

Exergy results are purely technical, and hence, they are not sufficient for policy and decision-makers as economic and environmental analysis also have a key role. Consequently, production costs found in the literature are also presented in this chapter for both first and second generation biofuels. As observed, it is not clear which is the most economical option as production costs are highly dependent on feedstocks prices as well as the production scale. Fischer-Tropsch process is especially sensible to the production scale, and it can only become competitive with fossil diesel at scales above 400MW_{th} or even more.

Environmental impact is another major issue when evaluating the sustainability of biowastes-to-biofuels conversion. Some experts have conducted an LCA analysis in order to evaluate the potential benefit of second generation biofuels over fossil fuels. In general, biofuels have lower GHG's emissions and use less non-renewable primary energy. However, some biofuels seem to have greater impact in other categories such as eutrophication, summer

smog, acidification and carcinogenic emissions. This is commonly explained by the fact that modern fuel cells cars are still more energy-intensive to produce.

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Chapter 5

AUTO-GASIFICATION OF BIOMASS

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ABSTRACT

Amongst the renewable energies, the biomass is the most important energy source. Because of its wide spread availability, renewable in nature and potential in neutral in relation to global warming, the potential of biomass to help to meet the world energy demand has been widely recognized. Three types of biomass are available, one generated during the processing of wood in timber mills another is energy plantation and third bio-residues generated during processing of agricultural produce. Among these, bio-residues are available in plenty and their disposal in a benign way always poses a problem. Combustion, Gasification and Biomethaisation are the process of extracting energy from the biomass. For power generation, gasification is found to be economically viable at all capacities. Gasification is a thermo chemical process of converting the solid combustible in the biomass using substiochiometric quantity of air above 900˚C.

The composition of biomass indicates that C, H and O contents are more or less same in all biomass. Bio-Oxygen available in every biomass is sufficient to convert the solid combustibles into a gaseous fuel. The composition of the producer gas is found to vary from biomass to biomass. This is attributed to the ash content in each biomass and its composition. Ash catalyses the reaction and brings down the gasification temperature below 600˚C. This paves way for auto-gasification of biomass namely thermo-chemical conversion of solid combustible in biomass into gaseous fuel using bio-oxygen and catalytic ash. The feasibility of auto-gasification of various bio-residues and wooden logs has been established. Kinetics and Mechanism of auto-gasification has been elucidated using Thermogravimetric Analysis (TGA) data obtained with static air or nitrogen. In bio-residues such as rice husks, bagasse, coir pith, poultry litter etc., the temperature is uniform due to high porosity and the gasification takes place continuously. In wooden

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logs the temperature is not uniform. Therefore drying, devolatization and gasification take place simultaneously.

Keywords: Auto-Gasification, rice husks, bagasse, coir pith, poultry litter.

NOMENCLATURE

E	-	Activation Energy, kJ/mole
k	-	reaction rate constant, min^{-1}
k_0	-	Arrhenius frequency factor, min^{-1}
M	-	Weight of component yet to be converted, gram
n	-	Order of the reaction
R	-	Gas constant, kJ/mole K
$-r_d$	-	Rate of reaction, gram/min
T	-	Temperature, °C or K
t	-	time, minute
w	-	Total weight yet to be converted in a particular zone at any time, grams
w_f	-	Total weight yet to be converted at the end of the zone, grams
α	-	Thermal diffusivity, mm^2 / minute

1. INTRODUCTION

Per capita energy consumption of any nation decides its standard of living, industrialization and economic growth. Developed countries consume more energy than developing and underdeveloped countries. Most of the developed countries use fossil fuel as their energy source and the per capita energy consumption is mostly based on electrical energy consumption. Energy demand increases with the desire for acquiring more and more comfort offering services and equipment by mankind.

Since the fossil fuel sources are limited and are getting depleted faster, the gap between demand and supply widens. Exploring the fossil fuel sources to meet the demand indiscriminately leads to environmental deterioration. The environment gets polluted resulting in global warming considerably.

Therefore the need for identifying the harnessing energy sources are benign to environment has become a must. Planning and execution of polices taking long term interest into account are important. One such alternate source is the renewable energy source. Solar, Wind and Bio energies are the main renewable energy sources. Every country is blessed with one or more of the above renewable energy sources considerably. The renewable energy potential in India is given in Table.1.

The energy and environment securities have become important to protect the sovereignty of any nation. Solar energy is the source for wind and bio energies while bio energy depends upon solar and wind energies. The main source for bio energy is biomass. Biomass gets generated by photosynthesis using solar energy and consuming CO_2 in air. Therefore biomass

is considered to be the best and maximum efficient way of storing solar energy while consuming CO_2 in air. Biomass is looked upon environmentally benign fuel source.

Table 1. Renewable Energy Potential in India

A. Grid-interactive renewable power		
1.	Biomass Power (Agro residues)	605.80 MW
2.	Wind Power	8757.40 MW
3.	Small Hydro Power (up to 25 MW)	2180.84 MW
4.	Cogeneration-bagasse	800.83 MW
5.	Waste to Energy	55.75 MW
6.	Solar Power	2.12 MW
	Sub Total (in MW) (A)	12,402.74 MW
B. Distributed renewable power		
7	Biomass Power / Cogen.(non-bagasse)	95.00 MW
8.	Biomass Gasifier	99.79 MWeq
9.	Waste-to- Energy	26.70 MWeq
10.	Solar PV Power Plants and Street Lights	7.72 MWp
11.	Aero-Generators/Hybrid Systems	0.72 MW
	Sub Total (B)	229.93 MWeq
	Total (A + B)	12,632.67 MW

Source: Ministry of New and Renewable Energy, Government of India (2008).

2. BIOMASS – RELIABLE ENERGY SOURCE?

Indiscriminate cutting down of trees for biomass supply would result in deforestation brining out inbalance in ecosystem. A judicial combination of growing and cutting down of trees should be achieved.

Short-Rotation Wood Crops (SRWC) established in brazil, New Zealand and Australia over the past 25 years equal about 50,000 km^2 . SRWC plantings in China may be in the range of 70,000-1,00,000 km^2. SRWC and other energy crops established in US and EU amount to less than 1000 km^2. With some exceptions (most notably in Sweden and Brazil), the SREC have been established for purposes other than as decided bio energy feed stocks, however, portions of the crops are (or are planned to be) used for bio energy production. New renewable energy incentives, green house gas emission targets, synergism with industrial waste management projects, and oil prices exceeding 60 \$ Bbl^{-1} (in 2005) are major drives for SRWC or energy crop based bio energy projects [1].

Several investigations have been carried out leading to energy plantation projects. Ever increasing population needs more and more spaces for living. Many agricultural fields are getting encroached for living. This reduces the available land for energy plantation

considerably. It is anticipated that biomass in sufficient quantity may not be available in future. Timber mill wastes alone would be the only biomass source in future.

3. BIO-RESIDUES – RELIABLE AND RENEWABLE ENERGY SOUR

However there is inexhaustible source for biomass in the forms of agricultural residues. These residues are generated while processing agricultural produces such as paddy, sugarcane, coir nuts, etc., Bio-residues such as rice husk, coir pith, bagasse, etc., are available at all times since they are by products of agro industries. Every year million of tons of these residues are produced.

In Thailand the biomass energy consumption has been increased by 68% whiled the GDP/capita was tripled during 1980-1996. The imported energy, which at present [2006] accounted for 7% of GDP. The amount of agricultural residues is about 61 million ton a year, of which 41 million ton, which is equivalent to about 426 PJ of energy, was unused. The most promising residues are rice husk, bagasse, oil palm residues and rubber wood residue, merely due to their availability at the mills, from which heat-power cogeneration is feasible. Biogas resources are from industrial wastewater and livestock manure, which have potential of 7800 and 13,000 TJ/year respectively [2].

Disposal of these residues pose a number of problems. They are bulky powder occupying more volume. Therefore transportation and storage are very expensive. To create space for dumping these residues generated very year, they have to be burnt. Burning with out heat recovery will be colossal waste of energy source.

4. AUTO-GASIFICATION – A MYTH OR REAL?

Recently Jarvinen, et. al., (2002) [3] have reported the studies on auto-gasification of a biofuel such as black liquor and have proved that char upto 40% can be converted by auto-gasification. Saastamoinen (1996) [4] has presented a detailed combustion model, which considers simultaneous pyrolysis and char conversion.

The reactivity of char is very important for complete gasification. A large reaction surface area with the catalytically inorganic constituents in the form of ash influences the reactivity of char [3]. The residence time available for CO_2 and H_2O to react with char is also very important. Higher residence time can be provided by having larger particles. In fact Jarvinen, et. al., (2002) [3] reported that the percentage conversion of char increased with particle size. Further they have observed that char conversion by H_2O dominates during devolatilization process.

It is quite evident from their studies that auto-gasification of biomass is feasible. The extent of char conversion depends upon the water formation during devolatilization. The availability of fuel oxygen and hydrogen controls the formation of water. Therefore, the composition of biomass should be the key factor for the auto-gasification process.

5. COMPONENTS OF BIOMASS

It is customary to report the content of moisture, volatile matter, fixed carbon and ash as proximate analysis. Table 2 gives the proximate analysis of 13 biomasses reported by Raveendran et al. [5]. Upon heating the biomass gets dried upto 120°C, devolatalized the volatile matter upto 350°C and gasified the char above 350°C. Therefore it is customary to classify the entire gasifier process as drying, devolatiliation and gasification. Depending upon the nature of environment inert or reactive prevailing during gasification the process is called pyrolysis for inert environment and gasification for reactive environment. Pyrolysis is the devolatilization of volatile matter in inert medium to produce pyrolytic liquids, solid char and gaseous fuel. The liquid product may also be upgraded to refined fuels. The solid char may be used as a fuel. The gaseous fuel is high in hydrocarbons with high calorific value. Since the bulk density and calorific values of pyrolytic liquid and solid char are very high they have high energy density compared to original mass [6]. When the environment is reactive (air) complete gasification of biomass takes place yielding gaseous fuel and ash.

Table 2. Proximate analysis of Biomasses (Raveendran et. al. [5])

S.N	Biomass	VM(daf) %	Ash (db) %	Fixed carbon (100 – VM) %
1	Bagasse	84.2	2.9	15.8
2	Coconut coir	82.8	0.9	17.2
3	Coconut shell	80.2	0.7	19.8
4	Coir pith	73.3	7.1	26.7
5	Corn cob	85.4	2.8	14.6
6	Corn stalks	80.1	6.8	19.9
7	cotton gin waste	88.0	5.4	12.0
8	Groundnut shell	83.0	5.9	17.0
9	Millet husk	80.7	18.1	19.3
10	Rice husk	81.6	23.5	18.4
11	Rice straw	80.2	19.8	19.8
12	Subabul wood	85.6	0.9	14.4
13	Wheat straw	83.9	11.2	16.1

Cellulose, Hemicellulose and Lignin and extractives are found to be the major components of biomass. Raveendran et al. (5) have reported the composition of biomass in terms of these components. Table 3 reproduces these results for 13 biomasses.

Table 3. Components of Biomass (Raveendran et. al. [5])

S. N.	Biomass	Ash	Holo cellulose	Cellulose	Hemi cellulose	Lignin	Extra ctives	Total (holo)	Total (hemi)
1	Bagasse	2.9	65.0	41.3	22.6	18.3	13.7	99.9	98.8
2	Coconut coir	0.8	67.0	47.7	25.9	17.8	6.8	111.7	99.0
3	Coconut shell	0.7	67.0	36.3	25.1	28.7	8.3	98.7	100.1
4	Coir pith	7.1	40.6	28.6	15.3	31.2	15.8	94.8	98.1
5	Corn cob	2.8	68.2	40.3	28.7	16.6	15.4	102.9	101.8
6	Corn stalks	6.8	63.5	42.7	23.6	17.5	9.8	97.6	100.5
7	Cotton gin waste	5.4	90.2	77.8	16.0	0.0	1.1	86.7	100.2
8	Groundnut shell	5.9	55.6	35.7	18.7	30.2	10.3	102.0	100.7
9	Millet husk	18.1	50.6	33.3	26.9	14.0	10.8	96.5	104.1
10	Rice husk	23.5	49.4	31.3	24.3	14.3	8.4	96.5	101.8
11	Rice straw	19.8	52.3	37.0	22.7	13.6	13.1	98.8	106.2
12	Subabul wood	0.9	65.9	39.8	24.0	24.7	9.7	101.2	99.0
13	Wheat straw	11.2	55.8	30.5	28.9	16.4	13.4	96.7	100.4

The thermal degradation of biomass and samples of cellulose, hemicellulose and lignin has been studied extensively using TG Analyzer. Most of the investigators have studied the effects of heating rates and temperature on pyrolysis using TG analyzer. Since the main objective of their studies is to get maximum char and combustible volatiles, TGA studies were reported to have been carried out in inert atmosphere with flowing nitrogen to purge out the product gases thus preventing the secondary reactions. Low heating rates with low final temperature were employed to achieve slow pyrolysis of biomass and samples of cellulose, hemicellulose and lignin.

Williams and Besler [7,8] have carried out TGA of wood and rice husks and samples of cellulose, hemicellulose and lignin at heating rates of 5, 20, 40 and 80 K / min with nitrogen flowing to purge out the product of gases.

The following observations were made at all heating rates:

- Hemicellulose represented by xylan decomposes between 220 and 320 ºC and continued heating upto 720 ºC resulted in yielding char approximately 20 wt% of the original hemicellulose

- Cellulose decomposes between 250 and 360 ºC and has yielded char approximately 8 wt% of the original cellulose after heating to 720 ºC
- Lignin undergoes gradual decomposition between 80 and 500 ºC yielding char 55 wt% of the original lignin after heating to 720 ºC

From the TGA data, DTG curves have been drawn at different heating rates for wood, cellulose, hemi cellulose and lignin. The following was observed:

- Only one temperature for maximum weight loss has been observed for hemicellulose, cellulose and lignin.
- Two temperatures for maximum weight losses were observed for wood (one closer to hemicellulose maximum temperature and the other to cellulose).
- As heating rate increases there is a lateral shift in the temperatures for maximum weight loss due to combined effects of heat transfer at the different heating rates and the kinetics of the decomposition resulting in delayed decomposition.

6. COMPOSITION OF BIOMASS

Every biomass has carbon, hydrogen and oxygen in major quantities. These are represented as ultimate analysis. Raveendran et al. [5] have reported the composition of 13 biomasses. These are reproduced in Table 4.

The chemical formula for the biomass is generally represented by CxHyOz. The coefficients of x, y and z are calculated for each of the biomass and are also given in Table 4 along with average values. Comparing the average value with those of individual biomass, it is evident that these coefficients are more or less same in all the cases. This observation is further supported by the closeness of calorific values of these biomasses given in Table 4.

7. UNDERSTANDING OF GASIFICATION

Before attempting further, the understanding of chemical composition of bio-mass and its characterization should be analyzed. As a first stage, the investigation is restricted to powdery bio-mass only due to the occurrence of uniform temperature for gasification.

Raveendran et. al., [5] have reported the ultimate analysis of various bio-mass along with ash composition. Using the data the percentage of carbon that could have been converted into carbon monoxide by oxygen available in the bio-mass was calculated and is given in the last column of Table 4. It is evident that 56.5% to 87% of carbon could have been converted depending upon the available of oxygen. 13 to 43.5% of carbon is yet to be converted. However it is noteworthy that carbon is also consumed in the formation of methane and hydrocarbon and in the water gas reaction. Therefore it is possible to gasify the bio-mass in the absence of air theoretically. The characterization of bio-mass would throw some more light on this.

Table 4. Ultimate analysis of Biomass (Raveendran et. al. [5])

S.N	Biomass	Ultimate Analysis (wt %)				HHV[a] (MJ/kg)	Density (kg/m^3)	x	Y	Z	% conversion of carbon
		C	H	N	O						
1	Bagasse	43.8	5.8	0.4	47.1	16.29	111	3.65	5.8	2.94	81
2	Coconut coir	47.6	5.7	0.2	45.6	14.67	151	3.97	5.7	2.85	72
3	Coconut shell	50.2	5.7	0.0	43.4	20.50	661	4.18	5.7	2.71	65
4	Coir pith	44.0	4.7	0.7	43.4	18.07	94	3.67	4.7	2.71	74
5	Corn cob	47.6	5.0	0.0	44.6	15.65	188	3.97	5.0	2.79	70
6	Corn stalks	41.9	5.3	0.0	46.0	16.54	129	3.49	5.3	2.88	82.3
7	cotton gin waste	42.7	6.0	0.1	49.5	17.48	109	3.56	6.0	3.10	87
8	Ground nut shell	48.3	5.7	0.8	39.4	18.65	299	4.03	5.7	2.46	61.2
9	Millet husk	42.7	6.0	0.1	33.0	17.48	201	3.56	6.0	2.063	58
10	Rice husk	38.9	5.1	0.6	32.0	15.29	617	3.24	5.1	2.0	62
11	Rice straw	36.9	5.0	0.4	37.9	16.78	259	3.08	5.0	2.37	82.4
12	Subabul wood	48.2	5.9	0.0	45.1	19.78	259	4.02	5.9	2.82	70.2
13	Wheat straw	47.5	5.4	0.1	35.8	17.99	222	3.96	5.4	2.24	56.5
Average		44.6	5.5	0.3	41.8	17.32	253.84	3.72	5.49	2.61	70.89

[a] Higher heating value.

The combustible solid matters such as carbon, hydrogen and oxygen are chemisorbed on the ash matrix uniformly. These elements may exist as compounds or as elements. However it is customary to represent by the chemical formula $C_xH_yO_z$. The components are uniformly distributed on the pores of the ash. The composition of ash reveals that the ash could be a catalyst that would decompose these compounds. Normally in a catalytic heterogeneous reaction, the reactants have to get chemisorbed on the surface of the catalyst first before reaction. The reaction products have to get desorbed leaving the active site for the reactant for further reaction.

However in the gasification of bio-mass the reactants are already available on the active sites. Once they are activated at high temperatures, the reaction starts between adsorbed components, releasing gaseous fuel. The role of catalyst is to provide alternate path for the reaction consuming less energy. Therefore the entire gasification may be looked upon as a catalytic decomposition of combustible matter in the bio-mass.

Many investigators have already established the role of ash as catalyst. Shafizadeh [9] has observed that the presence of even very low concentrations of impurity either catalyses or inhibits the degradation of cellulose and the presence of trace metals results in shifting to lower temperature for thermal decomposition of cellulose.

In-sik Byun et. al, [10] have reported that water gas shift reaction takes place at lower temperatures (200 – 300 °C) in the presence of copper/zinc/alumina catalyst.

From the foregoing review, the following observations could be arrived at:

1. Biomass is a compound consisting of C,H,O in major quantity.
2. These constituents are held as chemisorbed matter on the fibrous ash matrix.
3. The composition of C,H and O is more or less same in all biomasses.
4. The calorific values are also nearly same.
5. Yet the quality and quantity of gasification varies with biomass.
6. Environment results in pyrolysis or complete gasification of biomass.
7. Flow of medium increases the yield of char preventing secondary degradation reactions.
8. In porous biomass, the reaction could be taking place continuously due to uniform temperature.
9. In non-porous biomass or in lumps, drying, devolatilization and gasification takes place simultaneously due to non uniform temperature.
10. In practice size less than 2 mm, chemical reactions controls, between 2 to 60 mm, chemical reaction and heat transfer control and above 60 mm, heat transfer controls the gasification.
11. Heating rate influence the quality of gasification and quantity of products.
12. Every biomass has sufficient quantity of oxygen (bio-oxygen) to convert the solid combustible matter in it to gaseous fuel.
13. Ash catalyzes the gasification.
14. Porous biomasses are gasified completely into ash at temperatures less than 600°C.
15. In porous biomasses, thermo-chemical conversion of solid combustible matter into gaseous fuel by bio-oxygen and catalytic ash.
16. Gasification by bio-oxygen in the presence of ash is called “Auto-Gasification”

8. PLAUSIBLE MECHANISM OF AUTO-GASIFICATION

A bird's view on the heterogeneous catalytic reaction would help in understanding gasification better. In heterogeneous catalytic reaction, the following steps are taking place:

1. Diffusion of reactants through the gas film surrounding the catalytic particle.
2. Diffusion of reactants through the pores of the catalyst to the reaction sites.
3. Chemisorption of reactants on the reaction sites.
4. Reaction between the chemisorbed reactants on the reaction sites.
5. Desorption of products from the reaction sites making the sites available for fresh reactants to get chemisorbed.
6. Diffusion of products through the pores to the surface of the catalyst.
7. Diffusion of products through the gas film surrounding the catalyst particle.

Steps 1, 2, 6 and 7 are considered to be physical steps as no new compound is formed in these steps.

Steps 3, 4 and 5 are chemical steps producing new compounds. Since, all these steps are taking place in series, the slowest step is considered to be controlling the reaction.

The activity of the catalyst depends upon the number of sites and activity level in each site. The activity level of site decides the product distribution while number of sites determines the rate of reaction. Temperature has exponential effect on these factors.

From the observations made, the gasification may be viewed as a heterogeneous reaction catalysed by ash. The reactants may be chemisorbed on the ash catalyst.

Because of these Steps 1, 2 and 3 of heterogeneous catalysts will not be existing in the gasification. All other steps will be taking part in the reaction. The following phenomena may be assumed to be taking place in gasification:

1. Upon heating, the sites on the ash catalyst get activated.
2. Depending upon the temperature, the number of sites activated and their activity level vary.
3. Carbon, hydrogen and oxygen molecules chemisorbed on the ash matrix get reacted.
4. Depending upon the activity level of the site carbon, hydrogen and oxygen give rise to various composition of CO, CO_2, hydrocarbons, water, methane, etc.,
5. Char produced may react with water vapor to produce CO and H_2 in the presence of catalytic ash.
6. The products thus formed diffuse through pores in the catalytic ash.
7. The products further diffuse through the gas film surrounding the biomass.

If the product gases are swept away by purging gases such as N_2 or Argon, as and when they formed, then the secondary degradation such as conversion of carbon to CO and H_2 would not have taken place. Several investigators have reported this [7,8].

9. VARIABLES AFFECTING AUTO GASIFICATION

The variable affecting the rate of gasification of bio-residues are to be identified and quantified [Kirubakaran et. al] [11]. The variables are given below:

S.No	Variable	Characteristics	
1	Environment	Inert	Reactive
2	Size	Small	Big
3	Shape	Powdery	Lump
4	Structure	Porous	Non-porous
5	Flow of medium	Static	Continuous
6	Heating rate	Slow	Fast
7	Temperature	< 500ºC	> 500ºC
8	Ash	Catalytic	Non Catalytic

Since pyrolysis and gasification of biomass are thermo chemical processes, the temperature and rates of heating have pronounced effects on the weight loss of biomass. Thermo gravimetric analysis (TGA) measures and records the weight loss of sample biomass as the temperature is raised at desired uniform rate. In addition the effect of environment such as inert and reacting atmosphere with and without flowing can be studied. For determining the characteristics of pyrolysis and also kinetic parameters, TGA is used extensively. Kinetic parameters are calculated using the net weight loss with simplifying assumptions which do not necessarily correspond to the complex chemical reaction in the thermal degradation of biomass. However TGA data provide useful comparisons of reaction parameters such as temperature and heating rates.

9.1. Materials and Methods

Samples of rice husks, poultry litter, bagasse, saw dust and coir pith were collected and dried in the shadow to achieve a constant weight. The dried bio-residues were ground to a fine powder and sieved. The samples with size less than 0.5 mm were collected and stored in a double polythene cover and sealed to prevent moisture entering the bag.

Perkin Elmer Pyris 7 Thermogravimetric analyzer (TGA) was used to record the sample weight as a function of temperature continuously at a heating rate of 5 °C/min. Nitrogen at a flow rate of 50 ml/min was admitted whenever TGA studies were carried out in purging mode.

9.2. Environment

Generally it is observed that reactive environment (air/oxygen) results in complete gasification of biomass while inert environment (nitrogen/argon) aids devolatilization (pyrolysis) yielding more char. Pyrolysis of biomass has attracted the attention of many investigators [7,8])as it yields solid, liquid and gaseous fuel from biomass.

Commercial gasifiers employ air at substoichiometric quantity to generate producer gas. Depending upon the type of contact between biomass and air, the gasifier is called down draft, updraft or cross flow gasifier. Each type has its own advantages and disadvantages in generating quality producer gas. Thus the understanding on the effect of environment on gasification has come to the natural end. Hence the present gasifiers produce gases with low calorific values due to dilution by nitrogen.

The TGA analysis of poultry litter powder @ 5°C/min has been carried out with air purging as well as nitrogen purging. Air purging results ash whereas the nitrogen purging produces char. The Figure 1 shows the experiments results.

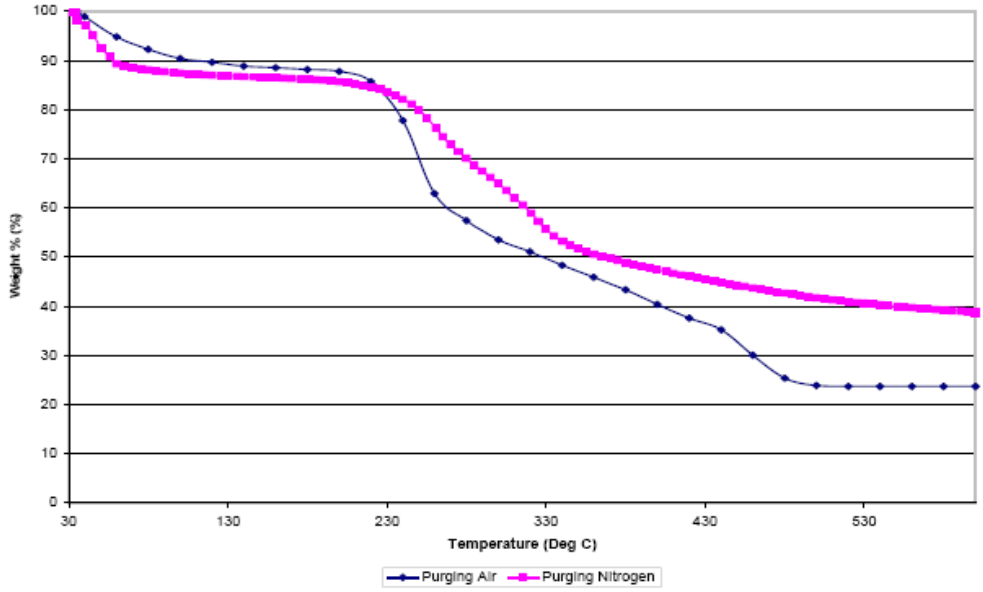

Figure 1. Temperature Vs Weight reduction of poultry litter in purging air and purging Nitrogen Environment @ 5°C/min heating rate.

9.3. Flow of Medium

Williams and Besler [7,8] have observed that the secondary degradation of char to gases can be prevented in pyrolysis of biomass by sweeping away the devolatilized gases by inert gases such as nitrogen. This yields more char equal to fixed carbon content in the biomass. Therefore many investigators have carried out the pyrolysis studies with flowing nitrogen.

Safi et al. [12] have carried out studies on global degradation kinetics of pine needles in air. An air flow rate of 50 ml/minute was maintained. The char obtained at different heating rates were less than the available fixed carbon, due to the presence of reactive medium such as air. If the medium were static, then there is a possibility of secondary degradation of char taking place. This may result in complete gasification of biomass. However no attempt is reported so far on the effect of static inert or reactive medium on the gasification of biomass.

The TGA analysis of poultry litter powder @ 5°C/min has been carried out with static nitrogen and purging nitrogen [Kirubakaran et. al] [13]. An interesting observation on TGA shows that in static nitrogen ash was obtained. It is shown in Figure 2.

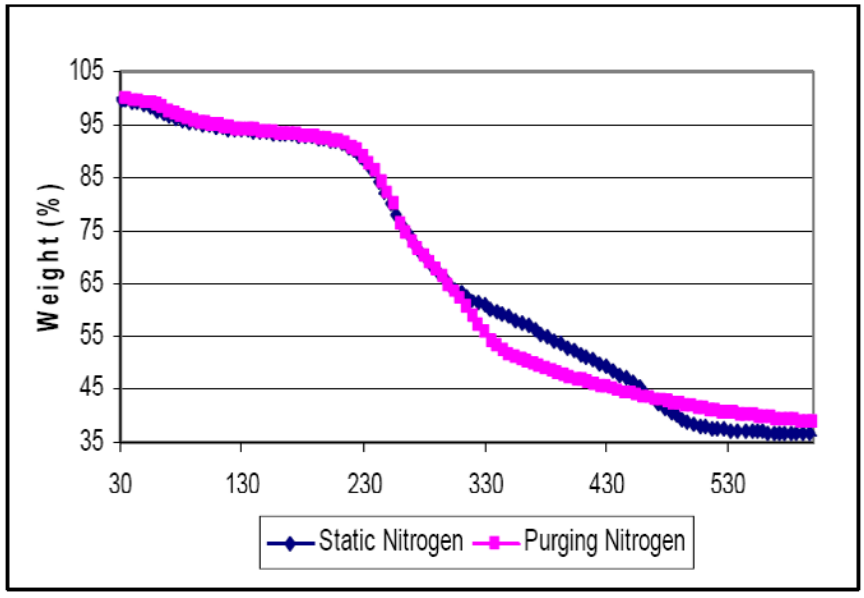

Figure 2. Temperature Vs Weight reduction of Poultry litter in Static Nitrogen and Purging Nitrogen Environment @ 5°C/min heating rate.

TGA analysis on static air also yields ash is given in Figure 3.

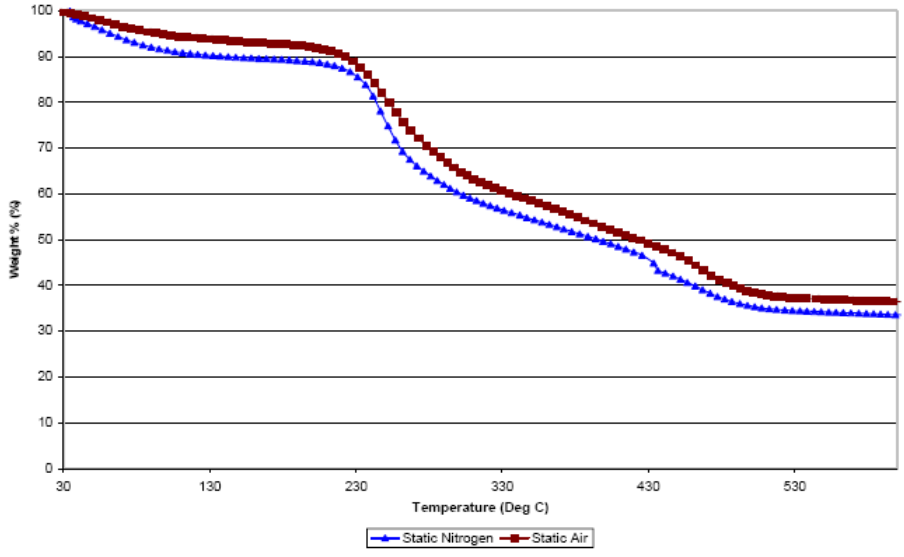

Figure 3. Temperature Vs Weight reduction of Poultry litter in Static Nitrogen and Static Air @ 5°C/min heating rate.

Figures 4 to 7 represent the TGA results obtained for rice husk bagasse, saw dust, and coir pith with static and purging nitrogen [14,15,16]. The following observations are made:

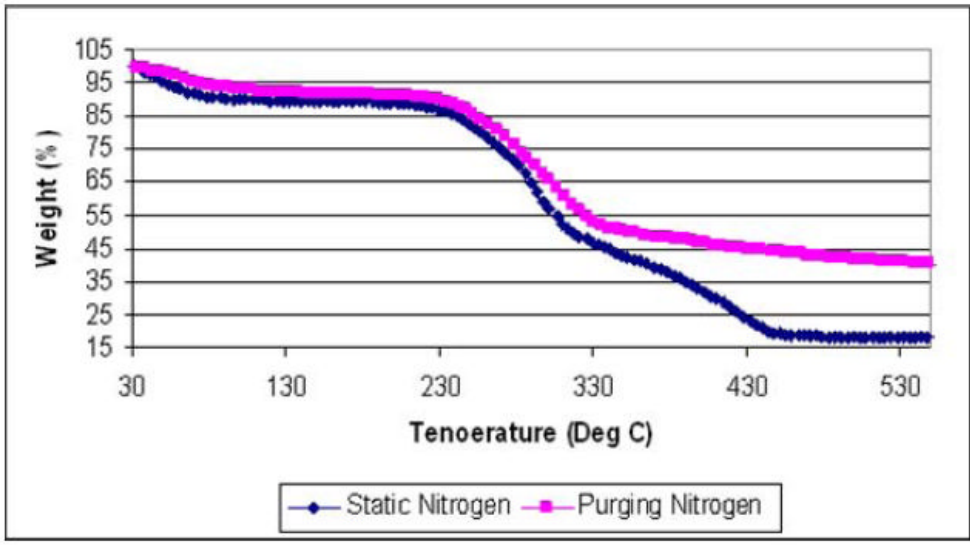

Figure 4. Temperature Vs Weight reduction of Rice husk in Static Nitrogen and Purging Nitrogen Environment @ 5°C/min heating rate.

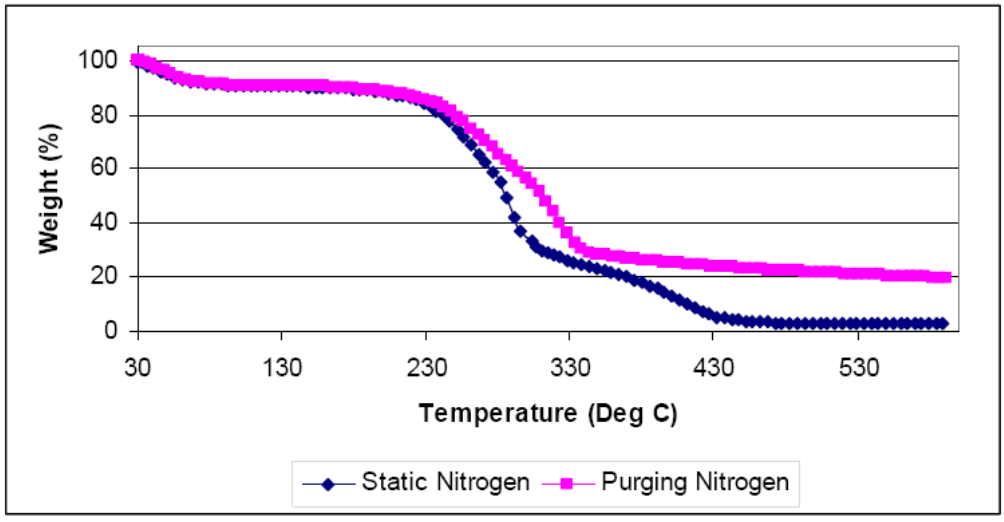

Figure 5. Temperature Vs Weight reduction of Bagasse in Static Nitrogen and Purging Nitrogen Environment @ 5°C/min heating rate.

The final % weight of biomass yet to be gasified is always higher with purging nitrogen than that with static nitrogen. This is attributed to the prevention of secondary reaction by purging nitrogen. It is worth to note from figures that in all the cases with static nitrogen, major quantities of bio-residues gets gasified by 430 °C, and by 550 °C, only ash results. This proves the complete gasification of bio-residue by the biomass oxygen. Further the static

nitrogen environment has made possible the secondary decomposition of char into gaseous products. Thus, the auto-gasification of bio-residues by the biomass oxygen is feasible. This has resulted in yielding producer gas with high specific calorific value due to the absence of any purging gas. The feasibility of complete gasification within 600 °C is attributed to the catalytic action of ash. At this temperature, ash is mostly in amorphous form with high reactivity.

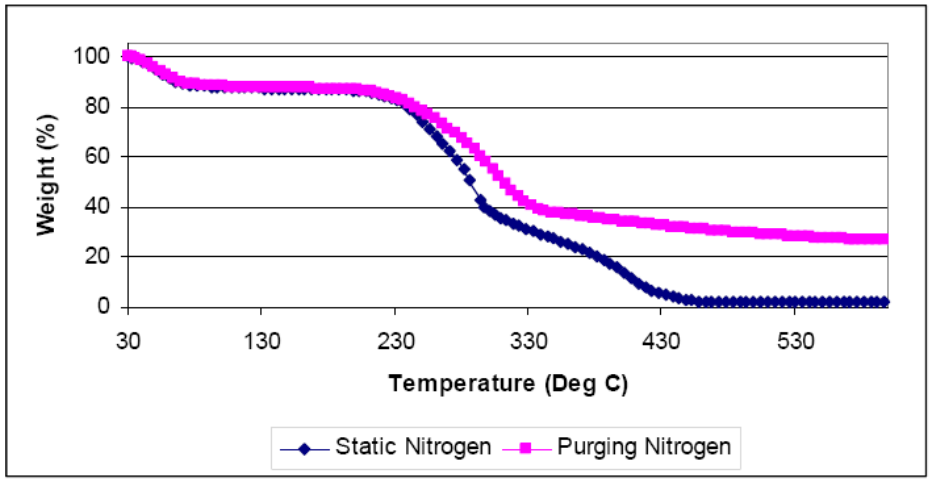

Figure 6. Temperature Vs Weight reduction of Saw dust in Static Nitrogen and Purging Nitrogen Environment @ 5°C/min heating rate.

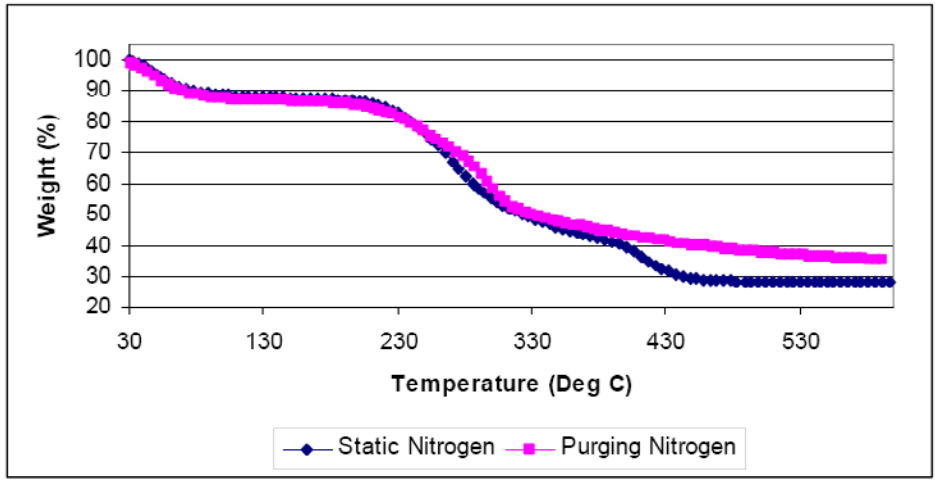

Figure 7. Temperature Vs Weight reduction of Coir pith in Static Nitrogen and Purging Nitrogen Environment @ 5°C/min heating rate.

9.4. Size and Shape

Smaller the biomass size better would be the heat transfer. The temperature would be uniform resulting in reaction taking place throughout the particle. Whenever reaction controls

the gasification, the rate of reaction will be maximum and increases exponentially with temperature. However there is a limitation on the size above which heat transfer would be controlling. Maa and Bailie [17] have shown that the pyrolysis of cellulose material is reaction-controlled for size less than 0.2 cm, for sizes 0.2 – 6 cm both heat transfer and reaction control, whilst above 6 cm heat transfer controls. Bio-residues are generally powder in nature. At present they are pelletized before gasification so as to reduce the volume of gasifier. Pelletization consumes power thus reducing the available energy. Lumps on the other hand can be gasified conveniently. However lumps beyond 6 cm size are not suitable. In order to have uniform rate of gasification yielding uniform composition of producer gas, the lumps are cut into small chips having size less than 2.5 cm. Chipping is also an energy consuming operation.

Several investigators (Galgano and Di Blasi [18]) have analyzed the course of gasification of wooden sticks in detail. Thermal conductivity plays a vital role in deciding the radial temperature profile. Since gasification is a thermal process, non-uniformity in temperature affects degree of gasification considerably. Therefore the bigger the particle size greater would be the non-uniformity in temperature. This leads to drying, devolatilization and gasification taking place simultaneously. This results in non-uniform gas composition with varying rate of reaction. The particle property evolves with the extent of reaction. The weight loss represents the sum of the individual losses due to three phases of gasification at a temperature averaged over the entire radius. The temperature increases from outer radius to centre. Each stage of thermal degradation of biomass takes place whenever the appropriate temperature is reached. For example around 100^0C drying releases water vapour creating more pores in the biomass. This change in particle property decreases the density and thermal conductivity. However the product / reacting gases can flow through there pores with least resistances. This shifts the regime of reaction from internal diffusion control initially to chemical reaction control. If the pore gets widened, then wall strength gets reduced .The wall of pores collapses once a critical thickness is reached.

The porosity corresponding to this thickness in called as critical porosity. The onset of peripheral percolation commences at this stage. In the early stages of reaction, the reaction in taking place at the external surface. Afterwards the shrinkage in particle size can be attributed exclusively to the peripheral percolation. The thermal degradation brings about changes in the particle property. Porosity and pore distribution change considerably resulting in variation in thermal conductivity and surface area. If the micro pores get widened and become mesa pore, the porosity increases with decrease in surface area. Increased pore size reduces the internal diffusion resistances and the regime of reaction is shifted to chemical control. The increase in porosity reduces the thermal conductivity and hence the heat transfer rate. At this stage, the onset of outer peripheral percolation collapses the fragments and the particle becomes devoid of the porous segments. Therefore the nature of influence of particle size on thermal degradation is highly complex. It depends upon the initial porosity, pore distribution, moisture and ash.

The TGA analysis of poultry litter @ 5°C/min has been carried out with static air at different particle size 100micron, <1mm particle size and >1mm particle size and reported in Figure 8. 100micron, and <1 mm particle yields ash with 530 °C where as more than 1mm particle yields ash after 700°C due to non uniformity in temperature in the particle.

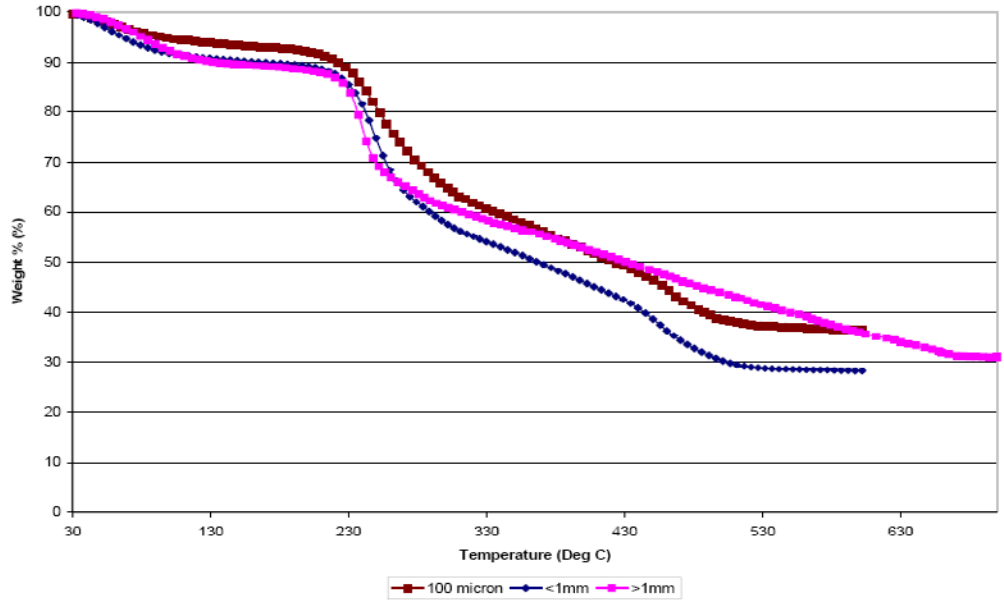

Figure 8. Temperature Vs Weight reduction of Poultry litter in Static Air @ 5°C/min heating rate for different particle size.

9.5. Structure

Whether the biomass is a lump or powder, the true porosity of the biomass is more or less same. If the biomass is highly porous, the surface area for reaction is very high and the diffusion of the reactant / product would be easy. Uniform temperature could be achieved throughout biomass resulting in continuous reaction at all portions of biomass yielding uniform composition of product gases. When the biomass is less porous and bigger in size, the temperature varies from the maximum at the exterior to the minimum at the interior. The reaction takes place only at the exterior surface. This surface shrinks with reaction. Because of the non-uniformity in temperature, drying, pyrolysis and gasification take place simultaneously yielding non-uniform composition of gases.

Grønli et al. [19] have studied thermo gravimetric analysis and devolatilization kinetics of hard woods such as alder, beech, birch and oak, and soft woods such as Douglas fir, pine A, pine B, redwood and spruce. They have observed that in the case of soft woods, the decomposition starts at lower temperature, the maximum temperature of weight loss for hemicellulose is higher and hemicellulose and cellulose zones are wider.

However for wooden sticks the dependency of auto gasification on the structure is discussed as follows:

If the initial porosity were low with micro pores then the biomass has very high surface area and thermal conductivity. The internal diffusion resistance and heat transfer rate would be high. The thermal degradation will be taking place only on the external surface. As the reaction progresses, the porosity increases due to widening of pores changing the pores to mesa pores. This reduces the surface area and hence the rate of reaction. Widening of pores reduces the wall thickness. The pore collapses once the porosity become critical. This shifts

the reaction regime from diffusion resistance to chemical reaction control. The reaction is attributed exclusively to the peripheral percolation.

If the initial porosity were low with mesa pores, then the biomass has low surface area and thermal conductivity. The internal diffusion resistance and the heat transfer rate would be low. The reactant gases diffuse throughout the particle easily. However, non-uniformity in temperature due to poor thermal conductivity is responsible for slowing down the reaction rate. Initially the reaction is taking place on the external surface, widening the pores further. Once the onset of percolation commences, the particle size shrinks reducing the internal diffusion resistance further. Therefore with low porosity and mesa pore particle, chemical reaction controls for a considerable amount of time.

If the initial porosity were high with micro pores, then surface area, thermal conductivity and strength parameter would be the highest. The internal diffusion resistance would be controlling. The higher heat transfer rates due to high thermal conductivity reduce the radial temperature variations considerably. The overall rate of thermal degradation would be always high. The strength parameter decreases with widening of pores and peripheral percolation commences as discussed earlier. Even though the reaction takes place on the external surface initially, the peripheral percolation controls the reaction further.

If the initial porosity were high with mesa pore the surface area, thermal conductivity and internal diffusion resistance would be the least. Chemical reaction is controlling always. With pore widening due to drying and devolatilization, the strength of the walls becomes reduced. Upon the onset of percolation, the wall collapses and the particle shrinkage is due to the peripheral percolation. Even though the gases diffuse uniformly, the reaction rate and mechanism are varying radially due to non-uniformity in temperature.

It is evident from the above discussion that the variations in initial porosity, pore distribution, ash content and its composition and moisture influence the thermal degradation of biomass combinedly and make the process very complex. In a wooden stick or lumps, these properties have pronounced effect on the temperature distribution. Temperature distribution decides the course of reaction. Temperature distribution depends upon thermal conductivity (k), specific heat (Cp), and density (ρ). All these are not constant and are changing with conversion. Therefore the variations with conversions should be understood first.

In porous solids, the thermal conductivity (k) is strongly dependent on the void fraction, the pore size and the fluid contained in the pores; in crystalline material the phase and crystallite size are important; in amorphous solids the degree of molecular orientation has considerable effect. Thermal conductivity (k) for non metals increases with temperature. (Bird et al. [20])

For non-porous solids, thermal conductivity (k) is a function of temperature, but not a strong one and is independent for a wide range of temperature gradients. For porous solids where radiation between particles becomes an important part of total heat flow the variations does not follow linear law. (Mc Cabe et al. [21])

Thermal conductivity (k) at room temperature for a considerable variety of wooden biomass may be accurately predicted from

$$k = \rho\,(0.1159 + 0.00233\,M) + 0.01375 \qquad (1)$$

where thermal conductivity (k) in B.t.u / hr ft ^{0}F, density (ρ) in gm /cc (based on weight when oven dry and volume when green) and the average moisture content (M) is in weight percent (Perry et al. [22]).

For M > 40%,

$$k = \rho\,(0.1159 + 0.00316\,M) + 0.01375 \tag{2}$$

Specific heat also increases with temperature in the similar way as thermal conductivity (k). Density (ρ) decreases marginally with temperature due to expansion of solid.

Thermal conductivity (k), specific heat (Cp) and density (ρ) are related by a quantity thermal diffusivity (α) (Bird et al. [20]).

$$\alpha = k / \rho\, Cp \tag{3}$$

Therefore thermal diffusivity (α) may be assumed to be independent of temperature for small temperature ranges.

The thermal diffusivities are generally calculated from thermal conductivity (k), specific heat (Cp), and density (ρ) using Equation (3)

It would be better if thermal diffusivity (α) is determined at the same operating conditions used for calculating conversion. Further thermal diffusivity (α) is influenced by method of heating. In actual gasifiers, there are different zones of varying temperatures. Wood, while moving from zone to zone, undergoes isothermal and non-isothermal heating during its journey to complete gasification. Under isothermal heating source, the exterior surface of wood is exposed to highest temperature, and as time progresses, temperature increases radially. In non-isothermal heating source, the temperature of wood increases gradually in radial direction. Depending upon the method of heating, the radial temperature profile varies resulting in different evolution of particle properties and conversion. Therefore thermal diffusivity (α) should be evaluated along with conversion.

Because of the non-uniform temperature distribution along the radius, drying devolatization and gasification of wood take place simultaneously yielding different weight losses at different radial positions. However, only the overall weight loss is estimated. Therefore the weight loss should be taken as that had occurred at an average temperature ($\overline{T}$) prevailing at that time. Therefore determination of average temperature is crucial.

Average temperatures ($\overline{T}$) at different time intervals are to be determined. Since thermal diffusivity (α) varies with average temperature ($\overline{T}$), it is possible to relate them using Fourier's law as follows:[21]

$$\frac{T_s - \overline{T}}{T_s - T_a} = 0.692 \times e^{-5.78 N_{FO}} \tag{4}$$

where,

$$N_{FO} = \frac{\alpha \times t}{r_m{}^2} \tag{5}$$

where,

α = Thermal diffusivity, mm^2 / minute

t = time, minute and

r_m = mean radius, mm

The effect of isothermal or non-isothermal heating on thermal diffusivity (α) at various times can be established for a given type of biomass. From the relationship thus established, thermal diffusivity (α) can be determined for any heating method at any time. The Fourier number (N_{FO}) can be determined at that time using Equation (5) and the corresponding average temperatures ($\overline{T}$) from Equation (1). Thus average temperatures ($\overline{T}$) at various times can be determined. The weight fraction yet to be converted (w) at any time can be obtained experimentally. And the corresponding average temperatures ($\overline{T}$) can be determined from thermal diffusivity (α). From weight fraction yet to be converted (w) versus time data, the rate (- rd) and rate constant (k) can be related. Using average temperatures ($\overline{T}$) and rate constant (k), the weight fraction yet to be converted of wooden stick can be determined at any time.

9.6. Heating Rates

Bridgewater [23] reported the influence of pyrolysis reaction parameters such as temperature and heating rates to determine the yield and composition of the derived products. In fast pyrolysis with high heating rates of upto 1000 ºC/min at temperature below 650 ºC and with rapid quenching the liquid, intermediate products of pyrolysis condenses without further breaking down higher molecular weight species into gaseous products. Formation of char is minimized by high heating rates. Gaseous products form at high heating rates to high maximum temperature. If the desired end product is the liquid hydrocarbon or bio-oil, fast pyrolysis is preferred. Fluidized bed, cyclonic, entrained flow, vortex and ablative reactors are recommended for fast pyrolysis.

Slow pyrolysis requires low heating rates and low maximum temperature. Maximum yield of char via secondary coking and repolymerization reaction is observed at slow heating rates coupled with a low final maximum temperature (less than 500 ºC) and with long gas and solid residence times. Therefore slow pyrolysis has been used for the production of char. Fixed bed reactor, multiple hearths and rotary kiln are used for slow pyrolysis.

Even though the rate of purging of gaseous products to prevent the secondary reaction influences the pyrolysis, no attempt has been made so far to evaluate its effect. William and Besler [8] have carried out a detailed study on the influence of temperature and heating rate on slow pyrolysis of biomass in a static batch reactor at heating rates of 5, 20, 40 and 80 K/min to a final temperature of 300, 420, 600 and 720 ºC with nitrogen as purging gas. Slow pyrolysis has yielded aqueous, oil, gas and char. The gaseous, liquid and solid products of pyrolysis are analyzed for composition, yield and calorific value.

The following is the observations made:

- A decrease in the yield of char and a corresponding increase in the yield of oil and gas resulted with increase in temperature for each heating rate.
- At 420 ºC and above, the aqueous yield remained virtually constant at about 37 wt%.
- Very high char yield has been obtained at 300 ºC as char has retained partially pyrolysed material such as hydrocarbons of high molecular weight.
- The high molecular weight hydrocarbon within char volatilizes and degrades thermally as the temperature was increased.
- The oil yield increases steadily from 300 to 720 ºC at all heating rates.
- The oils are highly oxygenated.
- An increase in carbon and hydrogen and a decrease in sulphur and oxygen contents of the oil with heating rates were observed.
- The gas yield also increases with temperature at all heating rates.
- The char yield decreases with temperature and with heating rates.
- The calorific values of oils and char were essentially independent of heating rates and were found to be an average 23 and 32 MJ/kg respectively.
- The yields of CO, CO_2, H_2 CH_4 and C_2H_6 increased with heating rates.
- Total calorific values were 13.6, 15.7, and 15.8 MJ/m^3 at heating rates of 5, 20, 40 and 80 K /min respectively.
- The calorific values of gases were fairly independent of heating rates above 5K/min.
- Water and oil were evolved throughout the higher temperature.

Safi et al. [12] have studied the global degradation kinetics of pine needles in air. TGA was carried out with 10 mg of sample wood in air flowing at 50 ml/minute at 5, 10, 15, 25 and 30 K /minute. It is interesting to note that three temperatures for maximum weight loss were observed unlike wood and rice husk pyrolysis reported by William and Besler [8]. Further there is a lateral shift in the temperatures for maximum weight loss for heating rates 5 and 10 K/min. The temperature for maximum weight loss decreases with increase in heating rates from 15 to 30 K/min. It is evident from the above that the heating rates influence the rate of gasification considerably.

Therefore TGA were carried out at heating rates of 5,10,15,20,30,40 and 50^oC/min in static air medium for poultry litter particle and reported in Figure 9. It is observed that beyond the heating rate of 15^oC, grayish or black ash was observed.

9.7. Temperature

Two temperature ranges are normally selected above and below 500 ºC. Generally temperatures above 500 ºC are chosen for reduction of carbon dioxide by carbon to carbon monoxide. Therefore pyrolysis of biomass is carried out at temperature less than 500 ºC for the maximum yield of char with inert medium flowing. Complete gasification is achieved at temperature above 500 ºC with air flowing.

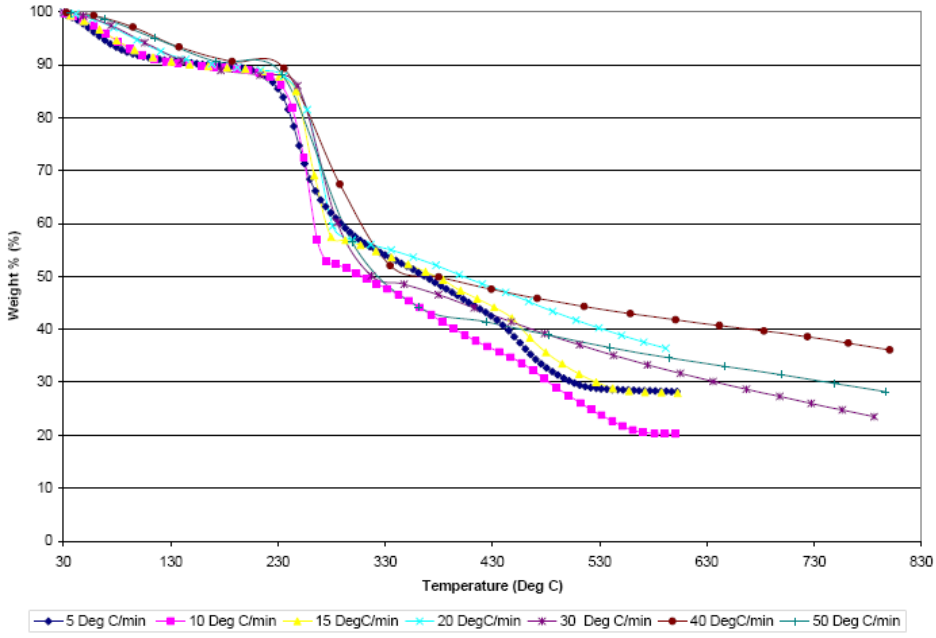

Figure 9. Temperature Vs Weight reduction of Poultry litter in Static Air at different heating rate.

9.8. Ash

Ash contains mineral matters. The composition of ash in bio residues as reported by Ravindran et al. [5] has been reproduced in Table 5. Shafzadeh [9] has observed that the presence of even very low concentrations of impurity have been shown to either catalyze or inhibit the degradation. Further the presence of trace metals results in shifts to lower temperature for the thermal decomposition of cellulose. In-Sik Byum et al [10] have reported that the oxides of copper / zinc / aluminum catalyze the water gas reaction at lower temperature (200-300°C). Raveendran et al. [5] have studied the influence of mineral matter on pyrolysis by demineralizing the biomass and then impregnating with salts and has reported the following:

1. In cases of demineralized coir pith, ground nut shell and rice husk, the char yield increases.
2. In cases of demineralized corn cob and wood, the char yield decreases.
3. Demineralized rice husk yielded higher char than coir pith and groundnut shell.
4. Liquid yield increases for all demineralized biomass.
5. Coir pith, ground nut shell and rice husk yield less char when the demeneralized biomass is impregnated with zinc chloride and potassium chloride salts.
6. In all cases, the liquid yield decreases and the gas yield increases due to salt impregnation.
7. Zinc chloride impregnation has increased the gas yield and has reduced liquid yield.
8. Higher the salt concentration, the lower is the liquid yield.
9. Only cation effects the changes in liquid and gaseous yield.

Table 5. Ash Composition of Major Biomass: (ppmw Dry Biomass) (Raveendran et. al. [5])

S.N	Biomass	Al	Ca	Fe	Mg	Na	K	P	Si	CO	Cr	Cu	Mn	Ni	S	Zn
1	Bagasse	-	1518	125	6261	93	2682	284	17340	-	-	18	9	16	60	16
2	Coconut coir	148	477	187	532	1758	2438	47	2990	0.6	2.0	68	4	2	64	25
3	Coconut shell	73	1501	115	389	1243	1965	94	256	0.5	0.3	5	1	13	35	9
4	Coir pith	1653	3126	837	8095	10564	26283	1170	13050	3.2	0.2	1239	27	22	476	40
5	Corn cob	-	182	24	1693	141	9366	445	9857	-	-	Trace	19	6	15	11
6	Corn stalks	1911	4686	518	5924	6463	32	2127	13400	8.0	11	32	12	13	564	32
7	Cotton gin waste	-	3737	746	4924	1298	7094	736	13000	-	-	Trace	38	10	58	22
8	Groundnut shell	3642	12970	1092	3547	467	17690	278	10960	2.3	6	11	44	11	299	52
9	Millet husk	-	6255	1020	11140	1427	3860	1267	150840	-	-	Trace	38	49	317	94
10	Rice husk	-	1793	533	1612	132	9061	337	220690	-	-	21	108	32	163	1244
11	Rice straw	-	4772	205	6283	5106	5402	752	174510	-	-	Trace	463	45	221	47
12	Subabul wood	-	6025	614	1170	92	614	100	195	-	-	1	2	1	66	40
13	Wheat straw	2455	7666	132	4329	7861	28930	214	44440	-	-	7	25	25	787	18

It is evident that from observations 1 to 4, that the absence of mineral matters due to deashing has yielded more char and liquid fuels. Observations 5 to 9, on the other hand establish a decrease in the yield of char and liquid fuels due to impregnation of deashed bio-residues by salts like zinc chloride.

From the composition of ash for various bio residues given in Table 5, it is seen that ash contains mainly oxides of metals. These metal oxides impregnated on porous silica in the ash, catalyze the gasification.

10. KINETICS OF AUTO-GASIFICATION

Thermogravimetric analysis (TGA) is widely used for studying the effect of heating on thermal degradation of chemicals. The weight fraction yet to be converted at any heating rate and environment is recorded at regular interval of time or temperature. The derivative thermogram (DTG) is also obtained from TGA data. For elucidating the kinetics and mechanism of thermal degradation, it is necessary to determine the reaction rate constant (k) and order of the reaction (n). Further the dependency of rate constant on temperature should be established by Arrhenius equation. Arrhenius frequency factor (k_0) and activation energy (E) are to be evaluated.

Accurate determination of these kinetic parameters (k_0, E and n) would result in elucidating the correct mechanism for understanding the correct course of reaction. Further these parameters enable the design of commercial reactors to be very reliable.

The kinetic parameters are estimated presently by dividing the entire temperature range into several zones and by assuming order of the reaction. These zones may represent the various thermal degradation stages. For example, in biomass gasification, these zones represent drying, devolatilization and gasification. The constituents of biomass is broadly grouped as moisture, hemicellulose, cellulose, lignin and ash. Deveolatilization represents thermal degradation of hemicellulose, cellulose and lignin at different temperature ranges. Char is the product of gasification [7,8] During the gasification, char is converted into gaseous fuel. Each stage of thermal degradation occurs at different temperature ranges, drying upto 120°C, devolatilization between 200 and 375°C and gasification above 375°C.

The order of the reaction is mostly assumed to be one and the constants E and k_0 are determined by trail and error for each zone [24]. The prediction of weight yet to be converted at any time or temperature is also very cumbersome.

The method proposed here overcomes all the above said drawbacks and enables the accurate determination of these kinetic parameters.

10.1. Development of Method

Depending upon the thermal degradation characteristics of substances, different constituent of the substances degrades in different temperature ranges. Identification of these ranges are very important. It is not possible to determine the number of zones and the corresponding temperature ranges using TGA data alone. However DTG data derived from TGA data could be used for this purpose.

On heating, each substance degrades differently depending upon its constituents. TGA shows a continuous reduction in total weight with increasing temperature or time. However DTG derived from TGA data gives the rate of reaction with respect to temperature or time and picturises the effect of temperature or time and weight yet to be converted at the rate. Therefore understanding of DTG data would become essential for the elucidation of kinetics of thermal degradation. Temperature or time affects the rate of degradation in several ways. Most commonly occurring relationships between weight yet to be converted and the rate are shown in Figure 10.

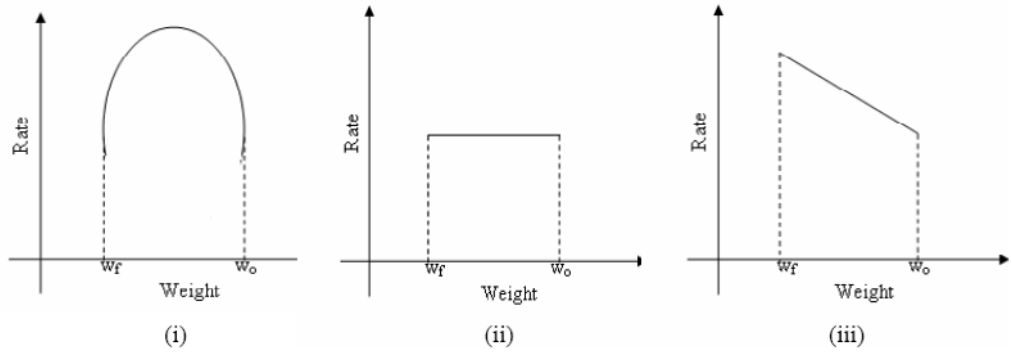

Figure 10. Shapes of rate Vs Weight relationship.

Depending upon the number of different compounds present in the degrading substance, one or all the above relationships may be observed.

The rate of reaction ($-r_d$) is given by

$$-r_d = k M_{avg}^{n} \quad (6)$$

where

M_{avg} - $(M_t + M_{t+1})/2$
M - Weight of compound yet to be converted
= $w-w_f$
w - Total weight yet to be converted in a particular zone at any time
w_f - Total weight yet to be converted at the end of the zone
n - Order of the reaction
k - Reaction rate constant

The reaction rate constant varies exponentially with temperature and is related by Arrhenius equation as follows:

$$k = k_0 e^{-E/RT} \quad (7)$$

where

k_0 - Arrhenius frequency factor
E - Activation Energy

R - Gas constant
T - $(T_{avg}+273)$ K

The non-isothermal rate of reaction is obtained by combining equations (6) and (7)

$$-r_d = k_0 e^{-E/RT} M_{avg}^{n} \quad (8)$$

At time t = 0, the weight of a particular compound yet to be converted is the highest and temperature is the least. As time progresses, temperature increases due to heating at a constant heating rate and weight yet to be converted decreases due to degradation. The rate constant k increases exponentially with temperature. The reduction in weight due to degradation tries to pull down the rate while the increase in temperature pulls up the rate constant k exponentially. The resultant rate increases for some time. At some point of time, the continuous depletion in the weight outweighs the benefit of higher temperature (and k) and the resultant rate decreases to a minimum. This results in the shape of rate Vs weight as shown in Fig.10 (i).

The rate of reaction is constant irrespect of weight and temperature. As explained for Fig 10 (i), k increases exponentially with temperature and weight decreases with progress of reaction. However the product of k and weight balances out the variation in such a way to maintain the rate of reaction constant [Fig 10 (ii)].

The rate of reaction decreases with weight. As time progresses, weight decreases while temperature increases. An exponential increase in k values due to increase in temperature outweighs the effect of decrease in weight and maintain a steady decrease in rate values with weight as shown in Fig.10 (iii).

However it is to be kept in mind that in all the above cases while weight decreasing with time (temperature), k keeps on increasing with temperature (time). The order of reaction, n plays a key role in maintaining these variations and retaining the relationship. It is important that the effect of temperature on k should be well defined by Arrhenius equation [25].

Therefore the following steps for estimating the correct order are followed:

1. For the various values of n = 0.5, 1, 1.5, 2, 2.5, and 3 determine rate constant k using –rd and M_{avg} in Equation (6)
2. Relate k and temperature using Arrhenius Equation (7)
3. For whichever order, a best fit for Arrhenius Equation is obtained that is the order of the reaction.

10.2. Demonstration of Model

The proposed method is demonstrated for the determination of kinetic parameters for the auto gasification of poultry litter at a heating rate of 5°C/min in static nitrogen medium. [26]. Figure 11 shows the TGA and DTG plot obtained.

Poultry litter contains moisture, hemi cellulose, cellulose, lignin, fixed carbon and ash. Upon heating, these compounds except ash undergo degradation at different temperature levels [26]. A close observation of DTG plot indicates several zones of degradation, each representing a compound. The negative values of derivative Weight % (%/min) are shown in Figure 11. However positive are taken for analysis.

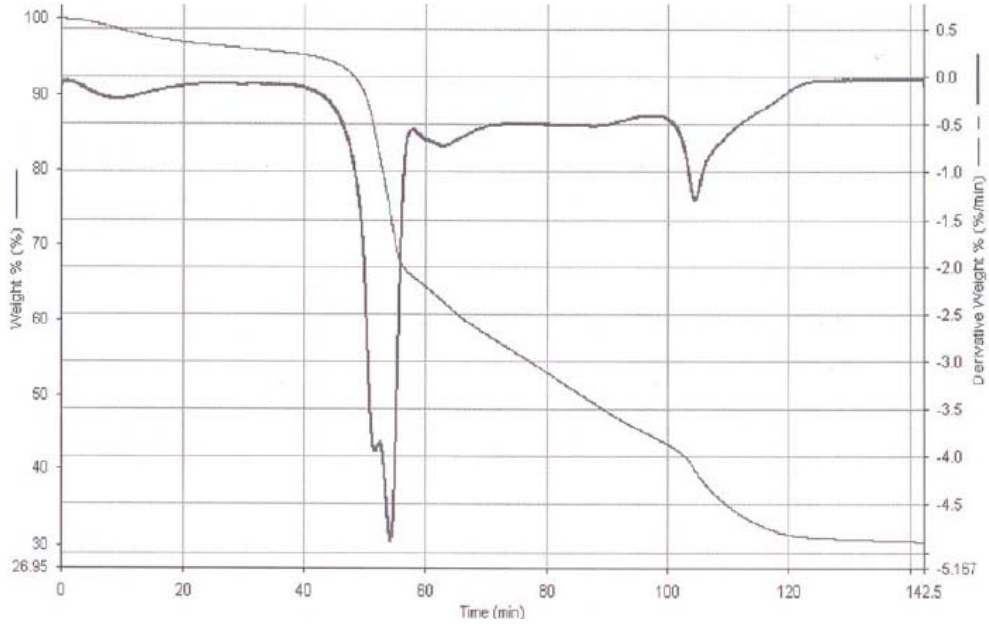

Figure 11. TGA and DTG plot for Poultry litter at 5 °C/min Heating rate in Static Nitrogen Medium.

Table 6 gives ranges of temperature, weight of individual compounds and the type of degradation. Explanations similar to Fig 10(i, ii and iii) can be offered to various zones

Table 6. Ranges of Temperature and Weight

Zone	Time Range, min		Temperature range, °C		Probable component	Total Weight of Component	Type of degradation
	From	To	From	To			
1	0	26	34	160	Moisture	0.1033	Figure 10 (i)
2	26	32	160	190	Volatiles	0.0053	Figure 10 (ii)
3	32	41	190	240	Hemi Cellulose	0.0527	Figure 10 (i)
4	41	47	240	265	Cellulose	0.1634	Figure 10 (i)
5	47	59	265	325	Lignin	0.1013	Figure 10 (i)
6	59	80	325	435	Volatiles	0.1255	Figure 10 (ii)
7	80	101	435	545	Char	0.1048	Figure 10(i)

The rate constants k, for the range of temperature in each zone are calculated for assumed orders of 0.5, 1, 1.5, 2, 2.5 and 3 by using Equation (8). The rate constant and the corresponding temperature for each order were related using Arrhenius equation [Equation (7)]. The Arrhenius constants were determined for each zone. Table 7 gives the values of k_0, E for various n for each zone along with regression coefficients. From the table, the best values of kinetic parameters for which the regression coefficient is the highest can be obtained. These values are given in bold types in Table 7.

Table 7. Values of Arrhenius parameters for various orders

S.No	Zone	Temperature Range °C	Order	E/R	k_{do}	Reg. Coeff.
			n	kJ/mole K	min^{-1}	R^2
1	1	34-160	3	24.5897	3.71352E+12	0.8703
			2.5	19.6904	5445198238	0.867
			2	14.7916	7984398.436	0.8603
			1.5	9.8923	11704.16453	0.8428
			1	4.9934	17.16204055	0.7653
			0.5	0.0942	0.025165029	0.0024
2	2	160-190	3	148.8438	1.32754E+49	0.8839
			2.5	125.1936	5.88023E+40	0.8841
			2	101.5476	2.61765E+32	0.8842
			1.5	77.8974	1.16528E+24	0.8845
			1	54.2514	5.18217E+15	0.8846
			0.5	30.6016	23068993.47	0.8831
3	3	190-240	3	117.7260	3.20173E+33	0.8379
			2.5	105.0378	2.40135E+29	0.8537
			2	92.3496	1.80E+25	0.8709
			1.5	79.6656	1.35217E+21	0.8938
			1	66.9774	1.01415E+17	0.9228
			0.5	54.2934	7.61393E+12	0.9583
4	4	240-265	3	266.6958	1.07982E+67	0.9255
			2.5	218.4084	4.66648E+54	0.927
			2	170.1168	2.03079E+42	0.9294
			1.5	121.8294	8.80247E+29	0.9335
			1	73.5378	3.81543E+17	0.9423
			0.5	25.2487	165379.8122	0.9685
5	5	265-325	3	163.7832	5.19536E+38	0.8506
			2.5	133.7448	2.02559E+31	0.845
			2	103.7064	7.90537E+23	0.8362
			1.5	73.6722	3.08527E+16	0.8199
			1	43.6338	1202898623	0.7804
			0.5	13.5937	49.36294295	0.571
6	6	325-435	3	64.2264	2.8275E+13	0.909
			2.5	53.9952	83323795034	0.9072
			2	43.7598	245301837.5	0.9044
			1.5	33.5278	722158.5557	0.8998
			1	23.2945	2125.580031	0.8906
			0.5	13.0607	6.258246287	0.8644
	7	435-540	3	202.7844	5.84804E+34	0.9583
			2.5	161.7294	2.65436E+27	0.9624
			2	120.6744	1.20599E+20	0.9683
			1.5	79.6194	5.47931E+12	0.9762
			1	38.5644	248948.1697	0.9634
			0.5	2.4906	0.011303985	0.0329

Best values are shown in bold types.

CONCLUSIONS

It is obvious from the discussion on gasification of bio-residues that auto-gasification of biomass into gaseous fuel by bio-oxygen and catalyst ash is feasible. The solid combustible matter and oxygen are chemisorbed uniformly on the ash matrix. Rising the temperature to a desired level would result in giving rise to various product gases due to auto-gasification. Maintenance of uniform temperature within the bio-mass is essential for the reaction. In order to establish the auto-gasification, TGA studies were carried out with powdery bio-residues such as rice husk, poultry litter, bagasse, saw dust, coir pith with static nitrogen and with purging nitrogen (50 ml/min) at a heating rate of 5 °C / min. With static nitrogen, ash has resulted in all the bio-residues while with purging nitrogen, ash and char have resulted. The static nitrogen environment allows the devolatilized gases to react with char further to complete the reaction while the purging nitrogen sweeps away the devolatilized gases as and when they formed thus preventing their subsequent reaction with char. Therefore it is possible to auto-gasify the powdery bio-residues completely.

However, thermal degradation of wooden sticks is influenced by the physical properties such as initial porosity, pore distribution, moisture and ash content. The effect of these properties on conversion has been discussed in detail. The combined effect of these properties can be attributed to a single parameter namely thermal diffusivity (α). Procedure to evaluate this parameter has been proposed. Following the procedure outlined, it is possible to determine the weight loss of wooden stick at any time under a given method of heating.

The existing procedure for the determination of kinetic parameters such as k_0, E and n for thermal degradation of substance is very cumbersome and does not give a clear picture on the degradation process. Eventhough TGA and DTG data are being used for the elucidation of kinetics and mechanism, generally the parameters k_0 and E are determined for an assumed order without justifying the assumption.

The proposed method eliminates these misgivings by dividing the degradation process in the entire range of time (or temperature) into various zones akin to DTG data. The combined effect of temperature and weight in deciding the rate curve has been explained for different shapes. For each shape of curve occurring in each zone, the rate constants are determined by assuming orders from 0.5 to 3 in steps of 0.5. Whichever order gives the best fit in Arrhenius plot, that is the order of reaction and the corresponding k_0 and E values are taken. The proposed method has been demonstrated successfully for the determination of kinetic parameters for the auto gasification of poultry litter at a heating rate of 5°C/min in static nitrogen medium.

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Chapter 6

BIOMASS GASIFICATION SYSTEMS INTEGRATED WITH FUEL CELLS AND MICROTURBINES

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ABSTRACT

Biomass has lately experienced appreciable attention as a potential substitute for fossil fuels in electric power production. Renewable biomass crops, industrial wood residues, and municipal wastes as fuels for production of electricity provide substantial reduction of environmental impact. High reactivity of biomass makes it comparatively easy to convert solid feedstock into gaseous fuel for subsequent use in a power generating system.

The gasification of biomass is a thermal treatment, which ensues in a high production of gaseous products and small amounts of char and ash. Steam reforming of hydrocarbons, partial oxidation of heavy oil residues, selected steam reforming of aromatic compounds, and gasification of coals and solid wastes to yield a mixture of H_2 and CO, accompanied by water-gas shift conversion to produce H_2 and CO_2, are well-proved processes. Biomass gasification derived gas is a renewable fuel, which can be used for fuel cell applications.

Fuel cells and microturbines are electricity producers that undertake relevant energetic and environmental performances. They feature high electricity to input chemical energy ratios and availableness of high temperature heat.

The positive properties of fuel cells and microturbines for high efficiency power generation at any scale and of biomass as a renewable energy source which is not intermittent, location-dependent or very unmanageable to store, indicate that a combined heat and power system consisting of a fuel cell integrated with a wood gasifier may provide a combination for delivering heat and electricity cleanly and efficiently. Integration of both technologies has been under probe for quite long time.

Fuel cell technology is one of the most interesting energy conversion systems offering nearly zero emissions, flexibility of operation and high conversion efficiency. Increasing demand for power and the depletion of fossil fuels are offering opportunities for the development of fuel cells as power generating systems. The aim of this chapter is

to assess the possibility of biomass exploitation for electric energy production in a given area.

Keywords: biomass gasification, distributed generation, fuel cells, gas turbine, hybrid systems.

NOMENCLATURE

a, b, c	Valve parameters
b_1, b_2	Parameters function of ignition temperature (K)
c_{pa}	Specific heat of air at constant pressure (J/kg K)
c_{pg}	Specific heat of combustion gases (J/kg K)
c_{ps}	Specific heat of steam (J/kg K)
E_0	Standard reversible cell potential (V)
e_1	Valve position
F	Faraday constant (C/kmol)
F_d	Fuel demand signal
i	stack current density (A/m^2)
I	Total stack current (A)
i_{0a}, i_{0c}	Anode and cathode current density (A/m^2)
K_6, a_1	Coefficients that depend on the HHV
k_f	Fuel system gain constant
k_{LHV}	Factor which depends on LHV
$LHV_{biomass}$	Lower heating value of biomass used (kJ/kg)
LHV_{fuel}	Lower heating value of fuel (kJ/kg)
m, n	Experimental constant (specific for SOFC)
$\dot{m}_{biomass}$	Biomass flow (kg/s)
$\dot{m}_{fuel}$	Fuel flow (kg/s)
N	Microturbine rotation speed (p.u.)
N_0	Number of cells in stack
N_a	Reactant flow to the anode (kmol/s)
n_e	Number of electrons exchanged in the electrochemical reaction
P_c	Compressor power consumption (W)
p_{cin}	air pressure at compressor inlet (Pa)
p_{cout}	air pressure at compressor outlet (Pa)
P_{FC}	Electrical power produced by fuel cell stack (W)
p_i	Partial pressure of specie i
P_{mec}	Mechanical power delivered by turbine (W)
P_{MG}	Mechanical power developed by microturbine (p.u.)
P_{MT}	Total mechanical power delivered by turbine (W)
P_T	Electric power output of turbine (W)
p_{Tin}	pressure of combustion gases at turbine inlet (Pa)

p_{Tout}	pressure of combustion gases at turbine outlet (Pa)
r	Effective ohmic resistance set of electrodes-electrolyte (Ω)
R	Universal gas constant (J/kmol K)
s	Laplace transform
T	Mechanical torque developed by microturbine (p.u.)
T_{cout}	Outlet air temperature (K)
T_E	Exhaust temperature of microturbine´s gases (K)
T_{FC}	Temperature ok fuel cell stack (K)
T_{is}	Temperature of injected steam (K)
T_{ref}	Exhaust temperature reference (K)
T_{Tin}	Turbine inlet gas temperature (K)
U_{fuel}	Fuel utilization
V_0	Reversible cell voltage
V_{FC}	Cell voltage (V)
V_{losses}	Total voltage losses (V)
w_a	Air mass flow into the compressor (kg/s)
w_f	Fuel mass flow (kg/s)
w_g	Turbine inlet gas temperature (K)
w_{is}	Injection steam mass flow (kg/s)
y_i	Mole fraction of fuel species *i* in the anode gas

Greek

ΔG_0	Change in Gibbs free energy (V)
Δh_{25}	Specific enthalpy of reaction at reference temperature of 25ºC (J/kg)
Δh_{IC}	Isentropic enthalpy change for a compression from p_{cin} to p_{cout} (J/kg)
Δh_{IT}	Isentropic enthalpy change for a gas expansion from p_{Tin} to p_{Tout} (J/kg)
ΔV_{act}	Activation losses (V)
ΔV_{conc}	Concentration losses (V)
ΔV_{ohm}	Ohmic polarization losses (V)
$\Delta\omega$	Rotation speed deviation of the turbine (rad/s)
η_c	Overall compressor efficiency
η_{FC}	Fuel cell efficiency
η_{FC+T}	Fuel cell and turbine generation system efficiency
η_T	Overall turbine efficiency
η_{trans}	Transmission efficiency from turbine to compressor
τ	Mechanical torque developed by microturbine (N m)
τ_f	Fuel system time constant (s)
ω	Rotation speed of the turbine (rad/s)

ABBREVIATIONS

CHP	Combined Heat and Power
DC	Direct Current

DG	Distributed Generation
GT	Gas Turbine
HHV	Higher Heating Value
HP	High-Pressure unit
IGCC	Integrated Gasification Combined Cycle
LHV	Lower Heating value
LP	Low-Pressure unit
MTG	Microturbine Generation
SECA	State Energy Conversion Alliance
SOFC	Solid Oxide Fuel Cell
TandD	Transmission and Distribution

1. INTRODUCTION

The economic development produces environmental and socioeconomic impacts, imbalances that force to define the sustainable development what guarantees the economic growth, the social progress and the rational use of the resources. The sustainable energetic development allows satisfying the energy present necessities without committing the necessities of the future generations, and the energy access for determined population's groups and territories.

As the oil crisis hit the western world in 1973, it became evident how vulnerable an energy system relying on a single source of primary energy can be. This fact, together with the predictions of some sources that the oil and natural gas resources would only last for some 40 and 60 years (Shahidehpour *et al*, 2005) led to an increased interest for developing energy conversion processes based on other sources of primary energy. The estimated number of years that oil and natural gas will be available is, however, debatable since the available statistics do not cover all the countries producing these fuels.

The first primary fuel source chosen for development was coal, partly because it has a predicted availability of more than 200 years, and partly because of an already existing knowledge of coal utilization as a fuel or for upgrading into more valuable products. As a result of these efforts, several large scale integrated gasification combined cycle (IGCC) power plants have been built both in Europe (Pruschek *et al*, 1995; Mendez *et al*, 1997), and in USA (Bissett and Strickland, 1991; Frey and Rubin, 1992). The basis in the systems is that coal is gasified, cleaned and utilized as a fuel in a power generation system combining both gas and steam turbines. At the same time some countries chose to start a similar development of gasification processes, now using biomass, i.e. wood chips, as the primary source of energy (Saenz *et al*, 1998). As a result of these activities, both designs and construction of several biomass-based systems deploying IGCC technique for power generation have been developed (Hughes and Larson, 1998; Newby *et al*., 1999; Newby *et al.*, 2000; Rhodes and Keith, 2005; Valero and Usón, 2006).

On the other hand, the Kyoto Protocol approved at the end of 1997 the global reduction of the emissions of gases. For European Union the commitment is to reduce in 2010 to 8%. Electric generation with renewable sources contributes of decisive way to the sustainable energetic development and to reach the commitments acquired in Kyoto. The European

Union's objective is to increase the contribution of renewable energy sources to 12 % of the total energy supplied by 2010. The Directive 2001/77/CE, force to countries members to adopt measures for production growth of electric power with renewable sources. Also, it noted that the main contribution for this execution could come from the biomass (IDAE, 2005; Directive 2001/77/EC, 2001).

The electricity production with renewable energies is completely linked with the distributed power generation that carries numerous benefits for the distribution network. Also, the use of biomass generate employment and wealth overall in rural areas, where it takes place, contributing to the sustainable development, being net zero level of CO_2 production. Nevertheless, and due to their particularities, it becomes necessary to prove that power generation from biomass is both technically and economically viable.

It has been largely accepted that biomass will represent a substantial role in the worldwide energy balance. The use of biomass for power generation has a potential of resolving, at least partially, the difficulty of non renewable fossil fuel depletion. Some countries are viewing biomass as a significant fuel for the power industry in the future and commit respectable resources to support research programs.

Gasification of solid fuels to generate a mix of H_2 and CO, followed by water-gas shift conversion to obtain H_2 and CO_2, are well-proved processes (Patil, 1987). Renewable biomass has also been considered as potential feedstock for gasification to produce H_2 and CO (syngas); the economics of present processes prefer the use of light hydrocarbons and coal. An alternative method to the production of H_2 from biomass starts with fast pyrolysis of biomass (Wang *et al.*, 1997). Production of hydrogen gas by gasification of carbon with superheated steam was described (Lower, 1963). The reacting carbon material is charcoal and is generated from wood (Wienhaus *et al.*, 1980), palm stones (Rabah *et al.*, 1983), or other domestic waste materials (Constantine, 1983).

Solid biomass has the highest potential (6 EJ/yr) for the power production from renewable energy sources. In addition, increasing attention is being given to the use of biomass for energy generation, in particular, by gasification since the produced fuel gas can be utilized in boilers, engines, gas turbines or fuel cells.

This chapter is organized as follows. In Section 2, general principles of distributed generation are explained. In Section 3, the use of forest residues is introduced. The gasification is explained in Section 4. State of the art of fuel cells and an electromechanical modeling of the solid oxide fuel cell (SOFC) are presented in Section 5. Section 6 presents a gas turbine model and the control configuration. Fuel cell and gas turbine hybrid systems are presented in Section 7, and finally, conclusions are provided in Section 8.

2. DISTRIBUTED GENERATION

The history of electric power generation systems has been derived from large central station plants due to the economics of scale. Fossil fuel plants have represented the majority of this power generation. According to tradition, there was strong yearly demand growth, which was stable at around 6-7%. Environmental issues and the oil crisis began to introduce new problems for the power industry in the 1970s. By the 1980s, these factor and changes in the economy had led to much smaller demand growth or around 1.6-3%. Simultaneously,

transmission and distribution (TandD) costs have grown from a historical level of 25% to around 150% of generation costs. TandD costs now represent almost two thirds of the capital expenditure budget for the utility industry. Thus, as a result of the reduced demand growth, increased TandD costs, intensified environmental concerns and various regulatory and technological changes, large central station plants are often impractical. The utility industry's generation paradigm is shifting from economies of scale to something that has been coined economies of mass production.

Due to the planned increments in fossil fuel usage, the greenhouse gas emissions of CO_2 to the atmosphere are considered to increase by about 60 % by 2015 over the 1990 level. The CO_2 produced from a given fuel per unit of power generated is inversely proportional to the thermal efficiency of a power plant, accepting complete utilization of the fuel. Additionally to CO_2, pollutants such as oxides of sulfur, oxides of nitrogen and unburned hydrocarbons are inclosed into the atmosphere when combustion is used to harness the chemically bound energy of the fuel. The quantity of pollutants emitted to the atmosphere which depend on the degree of pollution reprieve measures comprised, typically increase the plant operating and capital costs.

The principal energy source for power generation is worldwide constituted by fossil fuel. Particularly, in 1995, about 60% of the electricity power has been produced using natural gas, fuel oil and coal, while only 23% of the energy has been originated using renewable source (European Commission, 2006). The use of non-renewable source of energy leads to two main environmental disadvantages: greenhouse gas emissions and air pollution, in conjunction with the possible depletion of fossil fuels. These two problems can be decreased with a better use of energy resources, including a more rational employment of renewable ones, and realizing energy conversion devices with high conversion efficiency. Therefore, efficiency constitutes not only an indicator of careful treatment of natural fuel resource, but it acts even an indicator of air pollution to produce a reference amount of energy.

The imperativeness to reduce the encroachment on the environment of conventional energy conversion systems used for the generation of power and heat is increasing. Notwithstanding, energy demand is projected to increase and small-distributed power systems are appealing increased involvement.

The Distributed Generation (DG) is the generation of electricity by facilities sufficiently smaller than central generating plants as to allow interconnection at nearly any point in a power system. DG is not centrally planned, not centrally dispatched, usually connected to the distribution network and smaller than 50 – 100 MW (Dondi *et al*., 2002).

DG options can be renewable sources such as photovoltaic systems, high temperature thermal solar system, wind turbines, mini-hydraulics and biomass. This definition also comprises the conventional small generators, internal combustion engines, fuel cells and gas turbines. The major technical advantages of DG are the following (Barker and de Mello, 2000; Chiradeja and Ramakumar, 2004; CENER, 2007):

1. Reduced losses in the distribution network.
2. Improved voltage levels.
3. Environmental.
4. High efficiency.
5. Increased system reliability and security.
6. Improved power quality.

7. Increased distribution network capacity.

The economic benefits basically are:

1. Reduced investments.
2. Combined Heat and Power (CHP)
3. Reduced operation and maintenance costs.
4. Increased productivity
5. Reduced fuel costs due to increased overall efficiency.
6. Increased security for critical loads.

Available alternatives for biomass systems in the output range of 1 MWe include internal combustion engines, gas turbines and high temperature fuel cells. Hence, a motivation exists to produce energy efficient means of power generation while minimizing the environmental impact; gas turbines accommodate this promise. Moreover, distributed power generation which is attaining much attention from industry could be a niche market for fuels cells if simple systems can be determined so that the plant capital cost and the process controllability are not compromised.

3. USE OF FOREST RESIDUES

The biomass is the organic matter of biological origin usable for other goals different to the alimentary (energetic, industrial, etc). It constitutes a renewable resource; their main components are carbon, oxygen, hydrogen and nitrogen.

The forest residues constitute a form of biomass, they are originated by trees cut and are not habitually convertible in by-products, however can be used as organic fuel. They are obtained from the following operations previously planned:

- Works for enhancement of the forest mass.
- Fires prevention tasks. Mount cleaning, fire walls and cleaning of heaths are carried out.

The governments regulate the types of works to develop every year in determined areas according to the vegetation density, type of species, age, diameter, etc. After treatments the dispersed residues are generated. Later, residues are piling and burning (what is applied currently). The near residues to forest tracks or roads can be piled by cavalry or skidders.

The residues are not incinerated, and take advantage of their extraction and transport to generation plant. Therefore the works of biomass extraction would be integrated in the electric generation plant optimization. This doesn't suppose an increase of the cost, since the residues must be eliminated.

The forest residues are concentrated and transported beside the forest track or road. The main technologies are:

- Extraction and chipping
- Bundling and delivery to the power plant

Bundling technology compresses the residues by means of the formation of high-density packs; this reduces the delivery cost and minimizes its environmental impact. The principal machine is the forest packer. Consequently, it is possible to optimize store and transport using conventional forest equipment. The bundling machine works at the roadside, skidder is used to facilitate the packer's work (Velázquez, 2006).

The ported residues to generation plant are stored outdoors and before their usage as fuel they are subjected to drying, splinter and mill processes. Later, gasification and reformed take place for appropriate supply to generation system. The added advantages of the use would involve the reduction of plagues, smaller environmental impact and decrease in the possibilities of fires, etc.

Biomass is an important renewable energy resource. It not only has a wide distribution, but also abounds in quantity. However, biomass is one kind of resource distributed randomly with low energy density; it is difficult to deal with centrally on a large scale. Biomass gasification and power generation technology can reach reasonable efficiency at a certain scale, and provide high-quality power supply to the users, so it may be suitable for rural areas. In Spain, there is on one hand an enormous amount of biomass resources, mainly from the agricultural and forest sectors, and on the other hand there has been, for some time, insufficient electricity supply in rural areas.

4. GASIFICATION

Gasification is a century old technology that prospered quite considerably before and during the Second World War. The technology vanished soon after this war, when liquid fuel became advantageously available. Involvement in the gasification technology has experienced many ups and downs during the century. Nowadays, because of increased fuel prices and environmental problems, there is renewed interest in this old technology. Gasification has turned more advanced and quite a sophisticated technology.

The benefit of this technology is a decentralized energy conversion system that functions economically even for small scale. A gas producer is a mere device comprising of a cylindrical container with space for fuel, air inlet, gas exit, and grate. It can be constructed of fire bricks, steel, or concrete and oil barrels. The project of the gasifier depends upon the type of fuel used and whether the gasifier is portable or stationary. The gasifier alone is of limited use. The complete gasification system consists of the gasification unit (gasifier), the purification unit, and the burners.

Gasification is essentially a thermochemical process that converts biomass materials into their gaseous constituents. The outcomes of gasification are the producer gas, containing CO, H2, methane, and some other inert gases. Mixed with air, the producer gas can be used in gas turbines.

Based on the design of gasifiers and kind of fuels used, there exist different forms of gasifiers. Portable gasifiers are generally used for running vehicles. Stationary gasifiers combined with engines are mostly used in rural areas of developing countries for many proposes that include power generation and running irrigation pumps. Thus, these technologies are of great importance.

In theory, virtually all kinds of biomass with moisture content of 5-35% can be gasified, nevertheless, not every biomass fuel can conduce to productive gasification. Most of the developed work is carried out with common fuels such as coal, charcoal, and wood. It is accepted that fuel properties such as surface, size, and shape as well as moisture content, volatile matter, and carbon content determine gasification.

The keystone to a successful design of the gasifier is to realize the properties and thermal behavior of the fuel that is fed to the gasifier. Performance of the gasification system requires a versed and skilled operator. Compared to conventional systems, biomass gasification technology is inconvenient. However, it is economical in many places and may contribute to self-trust in the important time of a fuel crisis.

A large amount of research projects in the area of thermochemical conversion of biomass, mainly on pyrolysis, carbonization, and gasification, have been developed. The problems related to realization of process and utilization of the products have been recently reexamined (Baker *et al.*, 1987; Demirbaş, 2000a, Demirbaş, 2000b). In the literature a large number of experimental works regarding the gasification have been presented.

A wide research has been carried out on small- and medium-sized air gasifiers to obtain low BTU fuel gas and power (Rapagna *et al.*, 1992; Corella *et al.*, 1991). In the steaming reactor, hydrogen gas is released according to the following reaction at 1225 K:

$$2C + 3H_2O \rightarrow 3H_2 + CO_2 + CO \qquad (1)$$

The pyrolysis products comprise a volatile fraction consisting of gases, vapors, tar components, and a carbon-rich solid residue. The gasification of biomass is a thermal process that results in a high production of gaseous products and small quantities of char and ash. The pyrolysis of carbonaceous materials concerns to uncomplete thermal degradation leading to char, condensable liquid or tar, and gaseous products. In its most rigorous definition, pyrolysis is developed in the absence of air. Pyrolysis may be defined as that regime in which the same organic matter is degraded by thermal reactions in the absence of oxidizing agents to supply a complex volatile phase and a carbonaceous char incorporating inorganic components.

Some solids, liquids, and gases are originated in every thermal degradation process, including gasification. Nevertheless, pyrolysis is different from gasification (Maschio *et al.*, 1994) in that the products of pursuit are the char and liquids, which as a result of the incomplete nature of the process hold much of the structure, complexity, and signature of the raw material experiencing pyrolysis (Table 1).

Table 1. Values of the operating parameters

Process	Temperature (K)	Heating rate (K/s)	Solid residence time (s)	Water/biomass
Pyrolysis	675–875	0.1–1	600–2000	0.1–2
Fast pyrolysis	975–1225	250–300	1–3	0.2–0.6
Steam gasification	975–1225	300–500	0.5–2	0.8–2

With respect to wood, pyrolysis processes are alternately cited to as carbonization, wood distillation, or destructive distillation processes. As broadly admitted, carbonization refers to processes in which the char is the main product of interest (wood distillation, the liquid; and destructive distillation, both char and liquid).

A much less complicated and as a consequence, economically more interesting method of extracting oil from biomass is pyrolysis. This procedure carries off the need for a solvent recycle stream and possesses a higher thermal efficiency than the gasification phase of indirect liquefaction processes.

Pyrolysis of biomass is a complicated function of the experimental conditions under which the pyrolysis process moves. The most significant factors, which affect the production and composition of the volatile fraction liberated, are biomass species, chemical and structural composition of biomass, particle size, temperature, heating rate, atmosphere, pressure, and reactor configuration.

4.1. Gasification Process

The core of the gasification technology is the conversion of solid carbon fuels into carbon monoxide by a thermochemical process. The gasification of solid fuel is reached in an air sealed, closed chamber under light pressure relative to ambient pressure. The gasification process in general is explicated in this section. Gasification is actually a complex thermochemical process. Dividing of the gasifier into rigorously separate zones is not realistic, but however conceptually essential. Gasification stages happen at the same time in different parts of the gasifier (Kivisaari *et al.*, 2002).

Gasification is the word frequently used to identify the thermochemical processes that take place between a solid fuel and a gaseous reacting media, like air, oxygen or steam in order to obtain a combustible gas or synthesis gas rich in CO and H2. The variation compared to combustion is that the quantity of oxidant, i.e. oxygen in air or pure oxygen or steam, is not high enough to enable a complete oxidation, i.e. combustion. Alternatively, a partial oxidation, i.e. gasification, will take place. The whole gasification process can be separated into four steps, ensuing in a mixture of gaseous, liquid and solid products.

The first step is drying, where the wet of the fuel fed to the gasifier, coal or biomass, vaporizes. The second step where volatile chemical substances in the fuel evaporate is named devolatilization. This is accompanied by pyrolysis, the step where the greater part of the carbon content of the fuel is converted into gaseous compounds in the reduction area of the gasifier. The consequence of the pyrolysis is, aside from gases, a carbon rich solid residue named char. In the last step, called gasification, the char is in part oxidized into gaseous products and partly burnt to originate the heat required for the overall gasification process. Even though the reactions taking place during gasification are not very complicated and complex themselves, the unmanageable part is to show the kinetic relations between the different reactants.

The reactions taking place during the different steps of gasification are (Figure 1 and Figure 2):

Steam gasification: $$C + H_2O \rightarrow CO + H_2 \quad (2)$$

Water gas-shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$ (3)

Methanation reaction: $C + 2H_2 \rightarrow CH_4$ (4)

Methane reforming: $CH_4 + H_2O \rightarrow CO + 3H_2$ (5)

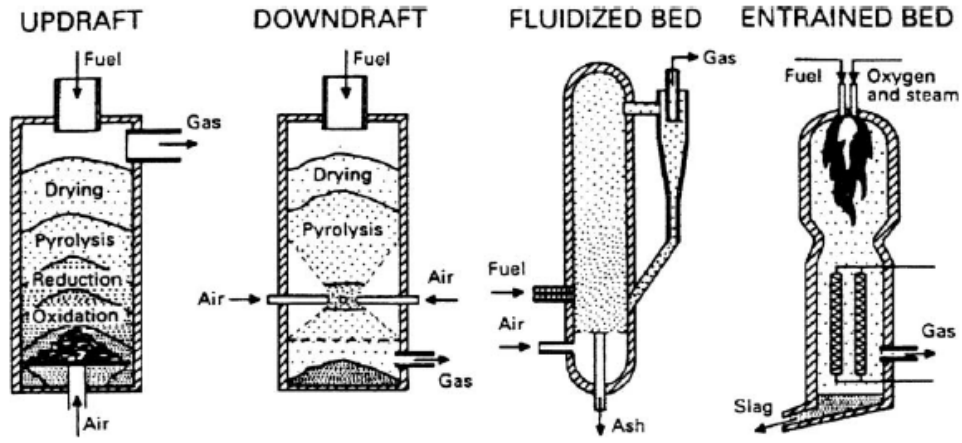

Figure 1. Different gasifier concepts.

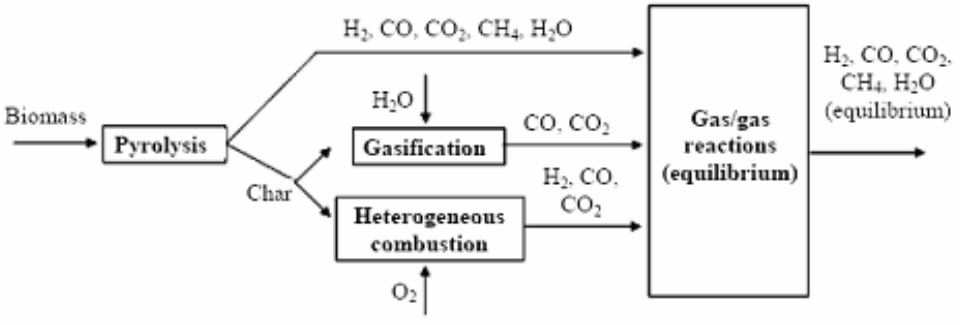

Figure 2. Scheme of chemical reactions.

4.2. Biomass Gasifier

As the pursuit for new energy conversion paths took off in the 1970s, the benefits of biomass gasification were recognized. The development way by many was to design biomass gasifiers by changing different types of existing coal gasifiers so that they could apply biomass instead of coal as their main fuel (Banerjee, 2006). The magnitude of the overall system generally decides the choice of which gasifier type to use, fixed bed, entrained bed or fluidized bed. For example, fixed bed gasifiers, depicted in Figure 1, are mostly used for small scale operation with gas engines, having an electrical output of about 80-500 kW (Mitchell *et al.*, 1995).

The principal difference between the updraft and downdraft fixed bed gasifiers is that in the first case, the product gas goes across the pyrolysis and drying zone of the fixed bed on its way out, leading in a product gas with higher contents of tars and higher hydrocarbons than for the downdraft gasifier, where the product gas goes through the hot zone where the tars and higher hydrocarbons are broke down. The entrained bed gasifier has encountered less use for biomass gasification, primarily because of the problems matched to the pulverizing of the biomass to be entrained with air (Kurkela *et al*., 1993). If, nevertheless, one wants to construct larger systems, the only real gasifier concept with a high enough biomass throughput for electricity production in the multi-MW scale is the fluidized bed gasifier (Mitchell *et al.*, 1995; Kurkela *et al.*, 1993), in a schematic manner displayed in Figure l.

All the gasifier types can work at either an atmospheric or high pressure. The advantage with pressurized functioning is mostly conceived to be that with increasing pressure, the gasifier and other operation equipment can be made smaller in size. The reward of atmospheric gasification, on the other hand, is that less energy is used-up by gas compression. When it comes to the selection of gasification media, there are two options, air or oxygen. Usually, the only cause for choosing oxygen is whether the produced gas is destined for synthesis gas or pipeline distribution (Mitchell *et al.*, 1995), differently it has been found to be inapplicable from both an economical, as well as an energetic point of view (Mitchell *et al.*, 1995; Kurkela *et al.*, 1993; Klosek *et al.*, 1994; Bain and Overend, 2002). Figure 3 illustrates a gasifier system.

Economic and energetic causes are not, even so, the only ones for using air as the gasification media for fluidized bed gasifiers operating with biomass. In order to run the gasifier properly, a high enough gas flow is required to achieve fluidization. If this were to be done with oxygen, steam would have to be used to dilute the oxygen, other than the result would only be combustion of the biomass. Since the heat of vaporization for water is high, the generation of steam would demand the use of heat that could be used for power generation in another place in the system. As air comes with a diluent, i.e. nitrogen, it has become the main alternative as biomass gasification media.

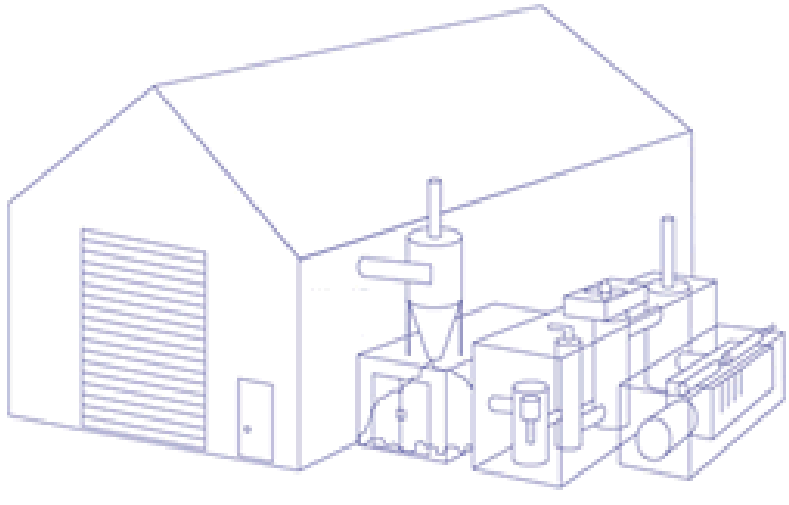

Figure 3. Schematic of a gasifier system.

The principal combustible constituents of wood are cellulose, hemicelluloses, and lignin, which are compounds of carbon, hydrogen, and oxygen. Other small combustible components in wood are fats, resins, and waxes. The principal non combustible component of wood is water, which makes up to 50% of recently cut wood. Although the ash content is low (<1%), because of high oxygen content, the calorific value is low (16-20 MJ/kg).

Nearest to charcoal, wood is quite an appropriate fuel for fixed bed gasifiers. Since wood includes high volatile matter, an updraft gasifier system produces gas incorporating tar, which needs to be cleaned out before utilization in engines. Cleaning of gas is a hard and labor-intensive process. Therefore wood is not desirable in updraft gasifier coupled with internal combustion engines. Notwithstanding, the gas containing tar from an updraft gasifier can be used for direct burning.

5. FUEL CELLS

During the past years, research and development actions in fuel cell technology have been stepped up within industry and universities. Therefore, fuel cells are now displacing towards commercial forwardness, or expecting a discovery within the next few years. Being an extensive technology, fuel cells are encountered with different designs and in several applications. The most important fields are small-scale power and heat generation, vehicle propulsion and portable purposes, such as substitutions for batteries. Having high efficiency, modular design and low noise these devices can represent an important role in next energy conversion. Nevertheless, problems such as cost are still the major barriers, although significant advances have been made in late years.

5.1. Basic Principles

In a fuel cell, the chemical energy incorporated in the fuel is converted directly to electricity (in direct current) and heat, as shown in Figure 4. The principles correspond a battery with the difference that fuel is provided continuously and power is developed as long as there is a fuel provision. The fuel cell was contrived in the nineteenth century by William Grove. Notwithstanding, the first real application was in the Apollo spacecraft in the past century when alkali fuel cells were employed to produce electricity (Blomen and Mugerwa, 1993). Evolution of SOFCs goes back to 1899 when Nernst reported zirconia as constituting conductive for oxygen ions (Larminie and Dicks, 2000).

Various types of fuel cells are under developing, such as solid polymer electrolyte (PEFC), alkali (AFC), phosphoric acid (PAFC), molten carbonate (MCFC) and solid oxide (SOFC) fuel cells. They are identified by the electrolyte used and the working temperature (with the MCFC and the SOFC being high-temperature. The PEFCs and AFCs are directed at mobile and portable applications, while the others are primarily destined for stationary power and heat generation. In late years much attention has been given to the SOFCs. Table 2 resumes the principal characteristics of the fuel cell discussed above (Seitarides *et al.*, 2008).

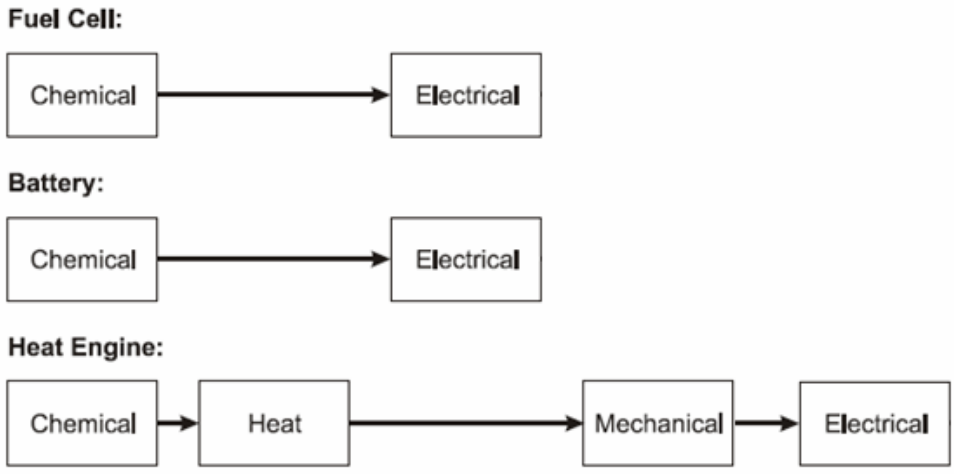

Figure 4. Energy conversion in a fuel cell.

Table 2. Fuel cell and characteristics

Fuel cell type	Electrolyte	Charge carrier	Anode reaction	Cathode reaction	Operating temperature	Electric efficiency (%)
AFC	KOH	OH^-	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$	60–120	35–55
PEMFC	Solid Polymer	H^+	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$	50–100	35–45
PAFC	Phosphoric Acid	H^+	$H_2 \rightarrow 2H^+ + 2e^-$	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$	220	40
MCFC	Lithium and potassium carbonate	CO_3^{2-}	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	650	>50
SOFC	Solid oxide (YSZ)	O^{2-}	$H_2 + O^2 \rightarrow H_2O + 2e^-$	$H_2 + O^2 \rightarrow H_2O + 2e^-$	1000	>50

Fuel cells can work on different fuels varying from hydrogen to gasified solid fuels, such as biomass. In all fuel cell, the fuel first has to be changed to a hydrogenrich gas. Hydrogen is currently the only fuel that can be oxidized electrochemically, maybe together with carbon monoxide. Research, nevertheless, is ongoing on direct-methanol (Murray *et al.*, 1999). Fuels from renewable origins are of particular importance for the future, but nowadays the most recognized for fuel cells is natural gas. More information on fuel cell can be encountered in (Blomen and Mugerwa, 1993) and (Larminie and Dicks, 2000)

Essentially, a fuel cell comprises of two porous electrodes separated by an ion-conducting electrolyte. The functioning principle of a SOFC is depicted in Figure 5. Hydrogen moves through the anode and reacts with oxygen. Throughout this reaction, water and heat are created, at the same time freeing electrons. The electrons go through an external circuit to the cathode, developing electrical power.

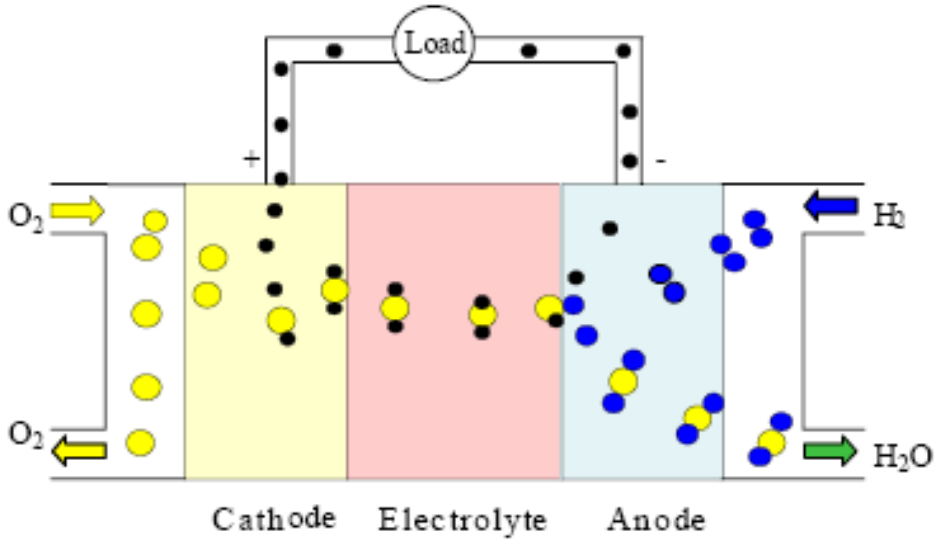

Figure 5. The principle of a SOFC.

In the cathode, oxygen moves through the electrode and the electrons are absorbed. Throughout this reaction, oxygen ions are constituted, which are carried through the electrolyte via empty spaces, ending the electric circuit. As the name indicates, the SOFC possesses a ceramic electrolyte, commonly yttria-stabilised zirconia (YSZ), which is a substance that conducts oxygen ions at temperatures above 800 °C (Larminie and Dicks, 2000). Materials usually employed for the anode and the cathode are nickel-YSZ-cermet and strontium doped lanthanum manganite, respectively. The interconnect links the anode of one cell to the cathode of the adjacent. The substance can be ceramic or metallic depending on the working temperature and fuel cell design. The cell is electrolyte-supported when working at about 1000 °C and electrode-supported when working at about 800 °C.

As shown in Table 2, the chemical reactions that occur within the SOFC are as follows:

$O_2 + 2e^- \rightarrow 1/2O^{2-}$	Cathode reaction	(6)
$H_2 + O^{2-} \rightarrow H_2O + 2e^-$	Anode reaction	(7)
$H_2 + 1/2O_2 \rightarrow H_2O$	Overall reaction	(8)

5.2. Fuel Cell Electrochemical Model

The electrochemical model of SOFC described in this chapter is based on a model developed by Padulles, Ault, and McDonald (Padullés *et al.*, 2000). The assumptions for the fuel cell model are as follows:

1. The gases are ideal.
2. The fuel cell is fed with hydrogen and air.

3. The electrode channels are small enough that the pressure drop across them is negligible.
4. The ratio of pressures between the inside and outside of the electrode channels is large enough to assume choked flow.
5. The fuel cell temperature is stable.
6. The Nernst equation applies.
7. The losses are as follows: activation, concentration and ohmic.

The upper limit theoretic work is the change in Gibbs free energy of the cell reaction, and the matching reversible voltage is the electromotive force given by the Nernst equation:

$$V_0 = N_0\left(-\frac{\Delta G_0}{RT_{FC}} + \frac{RT_{FC}}{n_e F}\left(\ln\frac{p_{H_2}p_{O_2}^{0.5}}{p_{H_2O}}\right)\right) = N_0\left(E_0 + \frac{RT_{FC}}{n_e F}\left(\ln\frac{p_{H_2}p_{O_2}^{0.5}}{p_{H_2O}}\right)\right) \quad (9)$$

where,

V_0	reversible cell voltage (V)
ΔG_0	change in Gibbs free energy (J/kmol)
E_0	standard reversible cell potential (V)
p_i	partial pressures of reacting species
R	universal gas constant (J/kmol K)
T_{FC}	temperature of fuel cell stack (K)
n_e	number of electrons changed in the electrochemical reaction
N_0	number of cells in stack

Due to irreversibility in the cell performance, the cell voltage, V_{FC}, is invariably lower than the ideal voltage, V_0. This deviation is called polarization and is the summation of three losses: activation, concentration and ohmic polarization.

$$V_{FC} = V_0 - V_{losses} \quad (10)$$

$$V_{losses} = \Delta V_{act} + \Delta V_{conc} + \Delta V_{ohm} \quad (11)$$

Activation losses: The general expression that represents the activation losses for both electrodes comes expressed by Butler-Volmer equation (Chan *et al.*, 2001)

$$\Delta V_{act} = \frac{2RT_{FC}}{n_e F} senh^{-1}\left(\frac{i}{2i_{0a}}\right) + \frac{2RT_{FC}}{n_e F} senh^{-1}\left(\frac{i}{2i_{0c}}\right) \quad (12)$$

where,

ΔV_{act}	activation losses (V)
i	stack current density (A/m^2)
i_{0a}	anode current density (A/m^2)
i_{0c}	cathode current density (A/m^2)
F	Faraday´s constant (C/kmol)

Concentration losses: There exist expressions proposed by Chan to calculate the concentration losses, both for cathode and anode, (Chan *et al.*, 2001), but in present chapter there has been adopted a more simplified empirical expression proposed by Hahn, (Hahn, 2000), and that gives us a good approximation of those losses.

$$\Delta V_{conc} = me^{\,ni} \tag{13}$$

where,

ΔV_{conc}	concentration losses (V)
i	stack current density (A/m^2)
m,n	experimental constant (specific for SOFC)

Ohmic polarization losses: In general, using the Ohm´s law, these losses can be defined according to Eq. (14).

$$\Delta V_{ohm} = rI \tag{14}$$

where,

ΔV_{ohm}	concentration losses (V)
I	total stack current (A)
r	effective ohmic resistance set of electrodes-electrolyte (Ω)

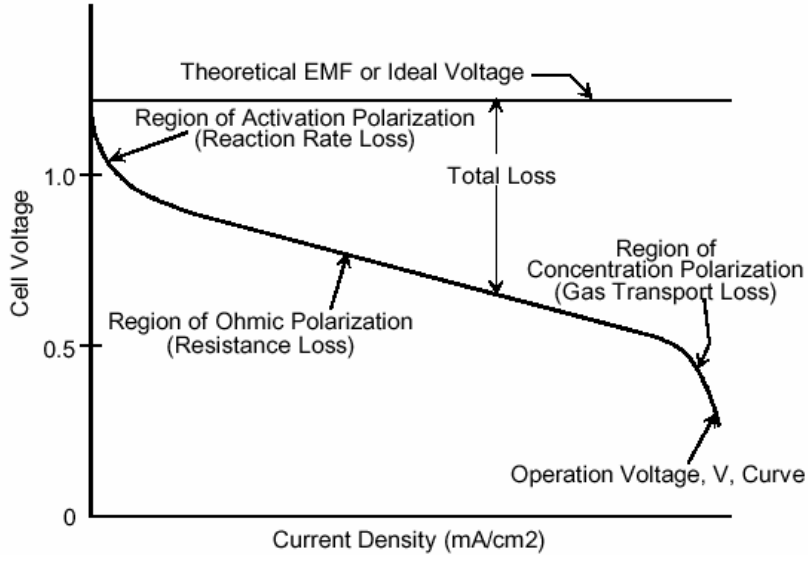

Figure 6. Current-Voltage characteristics of a fuel cell operating at 1073K.

As can be seen from Figure 6, each case of loss predominates at different operating ranges of the fuel cell. Polarization losses are caused by slowness of the reactions taking place at the electrode surface and may be considered as a reaction resistance. Consequently, polarization losses are related to the whole operating range, but they dominate for small current densities. Ohmic losses are induced by ohmic resistance in the cell materials, and they

are linearly dependent on current and current path. Ohmic losses in SOFCs are highly temperature dependent, particularly for the electrolyte, which is responsible for a greater fraction of the ohmic losses.

The efficiency of a fuel cell is calculated as the power divided by the *LHV* of the fuel:

$$\eta_{fc} = \frac{P_{FC}}{\dot{m}_{fuel} LHV_{fuel}} \tag{15}$$

where,

P_{FC} electrical power produced (in DC) by the fuel cell stack (W)

$\dot{m}_{fuel}$ fuel flow (kg/s)

LHV_{fuel} lower heating value of fuel (kJ/kg)

In this chapter, the fuel cell model uses a constant average cell voltage and a constant average fuel utilization to calculate the production of the fuel cells according to Faraday's law, equation 16:

$$P_{FC} = \left(\Sigma n_e y_i\right) U_{fuel} N_a F V_{FC} \tag{16}$$

where,

y_i mole fraction of fuel species *i* in the anode gas

U_{fuel} average fuel utilization

N_a reactant flow to the anode (kmol/s)

A Simulink model (MATLAB, 2005) was presented to simulate the fuel cell based on the analysis performed above (Figure 8). Figure. 10 and 11 show the voltage and power outputs of the model, respectively. The initial transients are due to startup of model and the initial conditions of the transfer functions being zero. It can be seen that the fuel cell produces approximately 120kW of power with a 360A current demand at steady state. The system delivers a voltage of 330V. The model use a stack consisting 384 fuel cells connected in series (Figure 9). The parameters used in the simulation are summarized in table 3.

Table 3. Simulation parameters for SOFC

Parameter	Representation	Value	Unit
P_{ref}	Reference power demanded by load	120	kW
V_{ref}	Reference net voltage of plant	330	V
T	Absolute temperature of fuel cell	1273	K
F	Faraday constant	96487000	$\frac{C}{kmol}$

Parameter	Representation	Value	Unit
R	Universal gas constant	8314	$\frac{J}{kmol.K}$
E_0	Standard reversible cell potential	1,18	V
N_0	Number of cells in stack	384	[-]
K_r	Constant, $K_r = \frac{N_0}{4F}$	$0{,}995 \cdot 10^{-6}$	$\frac{kmol}{s.A}$
U_{max}	Maximal utilization factor	0,9	[-]
U_{min}	Minimal utilization factor	0,7	[-]
U_{opt}	Optimal utilization factor	0,8	[-]
K_{H2}	Molar constant for hydrogen	$8{,}43 \cdot 10^{-4}$	$\frac{kmol}{s \cdot atm}$
K_{H2O}	Molar constant for water	$2{,}81 \cdot 10^{-4}$	$\frac{kmol}{s \cdot atm}$
K_{O2}	Molar constant for oxygen	$2{,}52 \cdot 10^{-3}$	$\frac{kmol}{s \cdot atm}$
τ_{H2}	Response time for hydrogen flow	26,1	s
τ_{H2O}	Response time for water flow	78,3	s
τ_{O2}	Response time for oxygen flow	2,91	s
r	Effective ohmic resistance	0,126	Ω
T_e	Electric response time	2,5	s
T_f	Fuel processor response time	5	s
n_e	Number of electrons exchanged	2	[-]
β	Rate of exchange for SOFC	0,5	[-]
i_{0a}	Anode current density	6.300	$\frac{A}{m^2}$
i_{0c}	Cathode current density	3.000	$\frac{A}{m^2}$
m	Experimental constant (concentration losses)	10^{-4}	V
n	Experimental constant (concentration losses)	$8 \cdot 10^{-4}$	$\frac{m^2}{A}$
A	Reaction area of fuel cell	0,6	m^2
r_{H_O}	Hydrogen-oxygen ratio	1,145	[-]
PF	Power factor	1,0	[-]
LHV_{H2}	Lower heating value of hydrogen	242.000	$\frac{kJ}{kmol}$

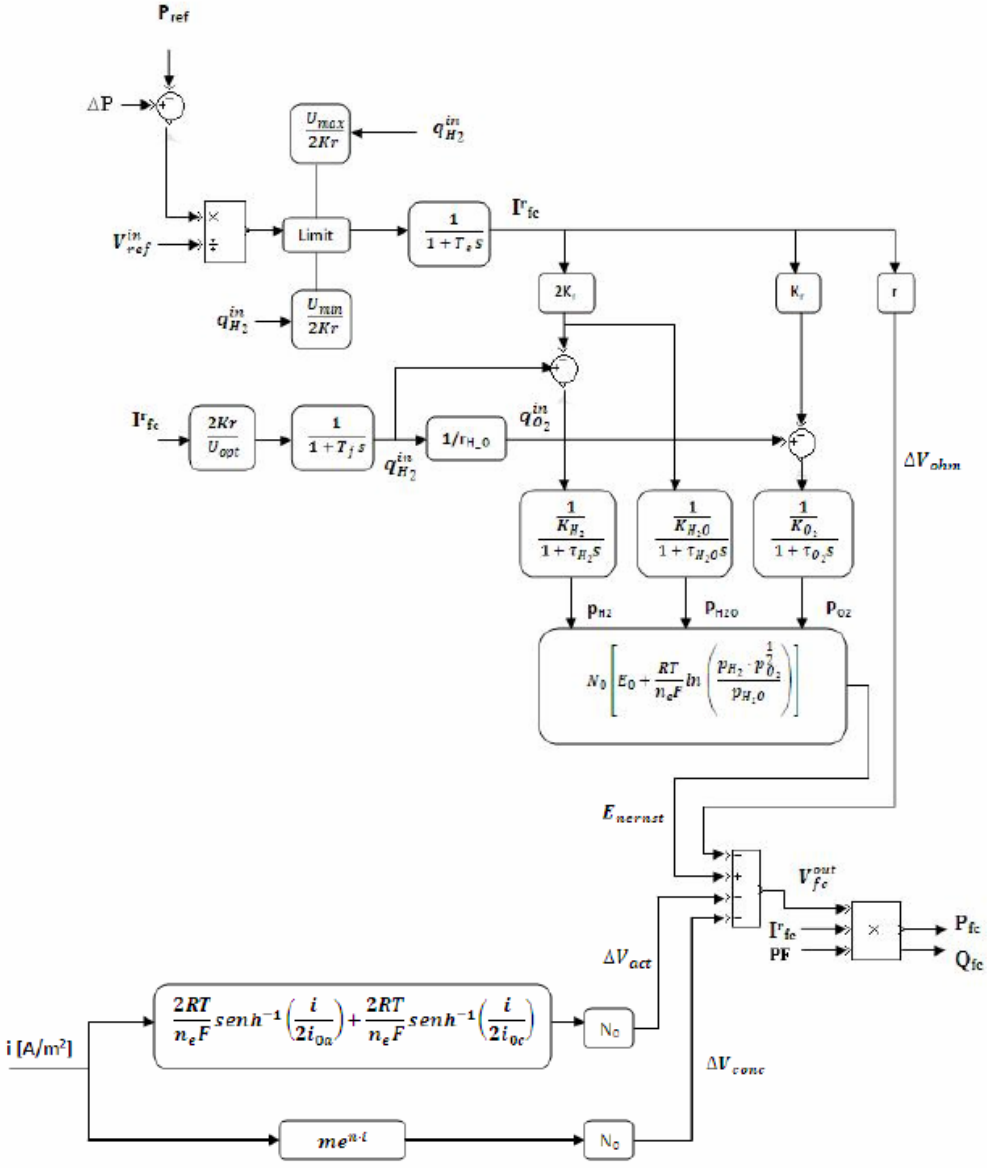

Figure 8. Simulink model of SOFC.

We can notice, in Figures 10 and 11, the voltage and power functions don´t obtain instantaneously, that is to say, there exists a delay of approximately 25 s. This is due to time responses of SOFC system.

The great inertia of the chemical reactions that takes place in the fuel cell originates the voltage of exit does not become stable even them 350 s approximately (Figure 10). The Rolls-Royce Company realizes important advances, managing to create prototypes based on fuel cells and batteries systems to solve this transitory problem.

In Figure 12, we can see the global efficiency of system generation based on SOFCs. The calculated efficiency corresponds with the Eq. (15) (using LHV of the H_2).

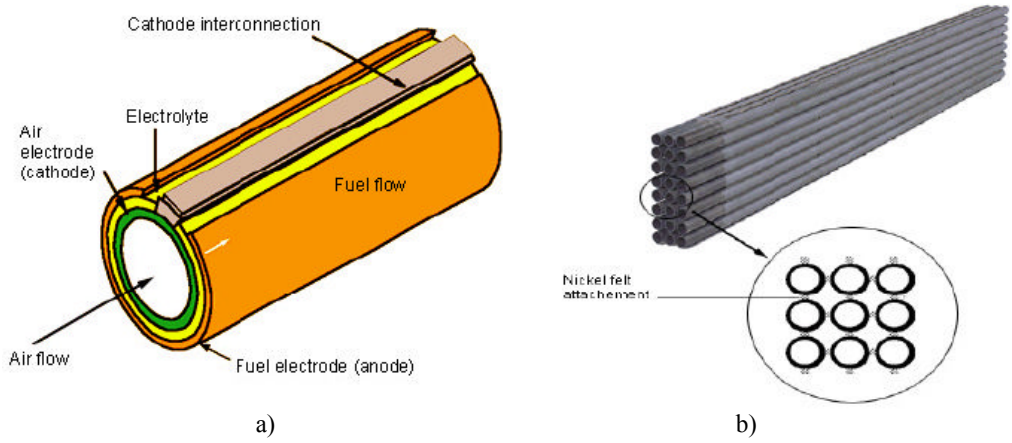

Figure 9. a) The tubular SOFC formulated by Siemens Westinghouse. b) Stack of the fuel cells connected in series.

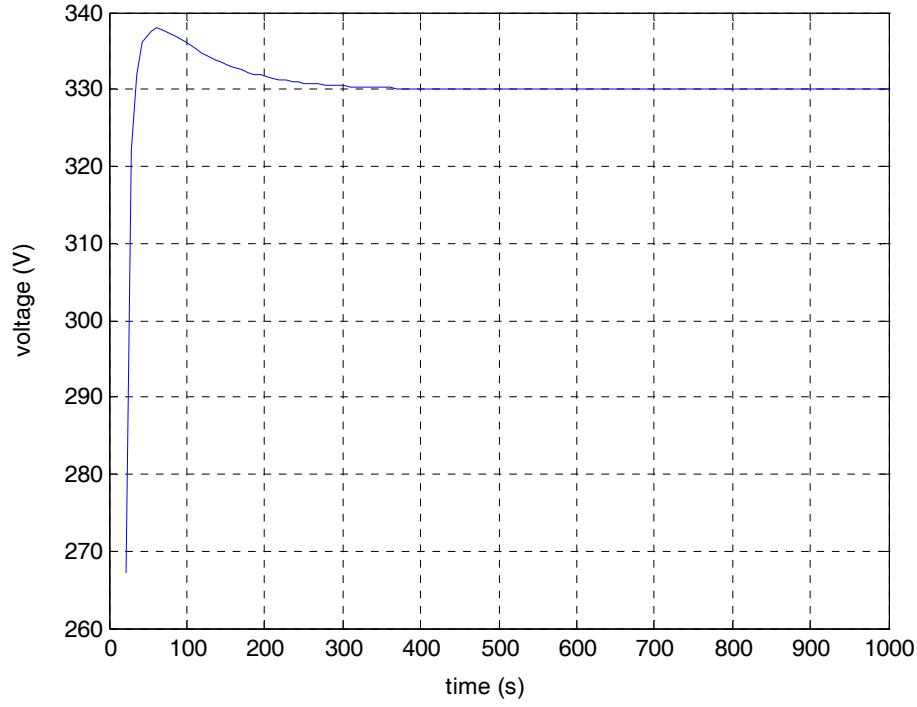

Figure 10. Fuel cell voltage (DC)

For a load of 120 kW (rated power), we can observe the system global efficiency is approximately 55 %. This efficiency is greater that obtained one in the conventional power plants by means of other technologies (Figure 13).

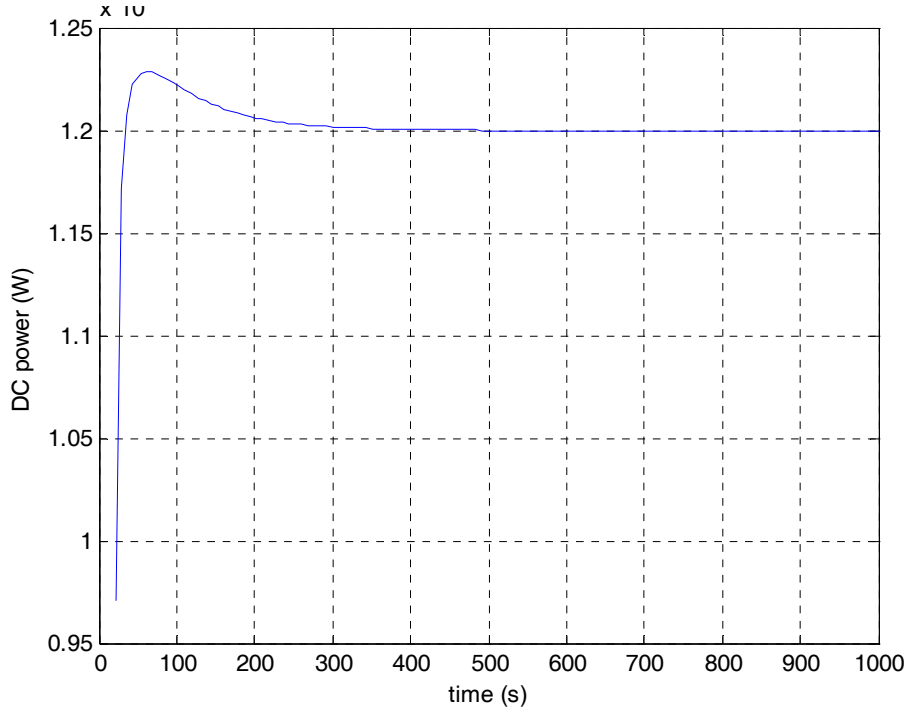

Figure 11. Fuel cell power output.

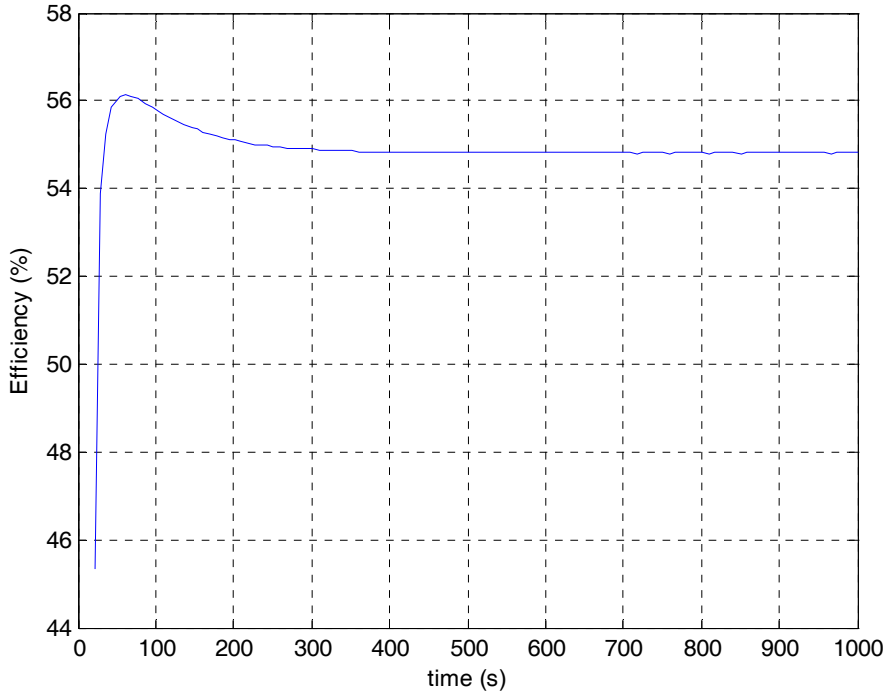

Figure 12. Fuel cell efficiency.

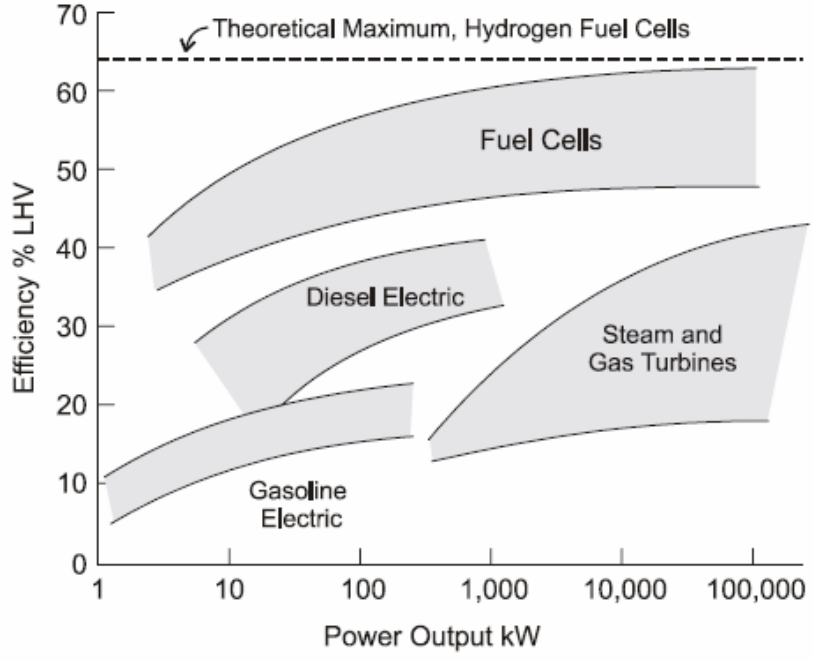

Figure 13. Comparison of efficiencies for electric power plants.

5.3. Biomass and Fuel Cell

A CHP system is employed to generate both electricity and heat. This system in this case is based on a fuel cell stack, and involves the integration of many components. The system has been assembled into three subsystems (Figure 14).

- Gasification: biomass feed is gasified to a gaseous product.
- Gas cleanup: the producer gas is cleaned and established.
- Fuel cell: cleaned fuel is reformed and, generating electricity and heat.

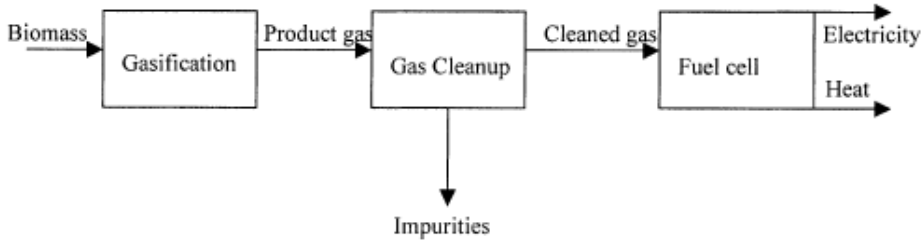

Figure 14. System configuration.

Biomass gasification is a technology for developing low-medium calorific gas from biomass. Gasification of biomass produces a gas consisting principally of H_2, CO, CO_2, CH_4, N_2 and light hydrocarbons. The composition of the gas changes depending on the biomass used, the gasification technology and the medium used during gasification. Table 4

(Seitarides *et al.*, 2008) supplies an overview of typical gasification gas compositions. Gasification processes using air develops a fuel gas, with N_2 content up to 50 vol%. Steam gasification originates a gas richer in H_2 and CO and with a low N_2 content. This gasification is therefore suited for an integrated system with SOFC. A flow diagram of the integrated process is showed in Figure 15 (Athanasiou *et al.*, 2007). In accompaniment with the gasifier and the SOFC, the process required a biogas reformer, a burner for the combustion of solid residue, a steam turbine and the indispensable heat exchangers.

Table 4. Biomass gasification gas compositions

Material	Medium	T (°C)	H_2	O_2	$CH_4+C_2H_x$	CO	CO_2
Pine sawdust	Air	800	32.22	0.57	8.34	42.96	15.91
Crushed almond shells	Steam	820	47.5	—	6.2	32	14.3
Pine	Steam	800	34.4		12.15	40.3	13.15
Helm oak	Steam	800	42.13		8.92	29.75	19.2
Wheat straw	Air/Steam	697	20.96	0.33	22.15	35.6	20.96
Wheat straw	Air/Steam	660	18.7	0.864	21.336	27.4	31.7
Wheat straw	Air/Steam	609	21.1	2.16	22.27	23.84	30.63
Wheat straw	Air/Steam	766	18.27	11.33	19.82	33.33	17.25
Wheat straw	Air/Steam	740	18.46	6.45	18.79	26.57	29.73
Wheat straw	Air/Steam	672	21.45	8.3	19.18	20.1	30.97
Wheat straw	Air/Steam	816	20.8	3.03	21.43	33.33	21.41
Wheat straw	Air/Steam	792	19.06	7.75	18.27	25.04	29.88
Wheat straw	Air/Steam	719	21.07	3.58	17.66	18.83	38.86
Pinewood chips	Air	780–830	22	—	15.31	33.36	29.33
Cynara cardunculus L	Steam	650	52.1	—	3.51	17.9	25.4
Cynara cardunculus L	Steam	700	58.7	—	3.8	17.1	20.3
Cynara cardunculus L	Steam	750	60.0	—	3.7	18.3	18.1
Cynara cardunculus L	Steam	800	60.4	—	3.9	19.0	16.6

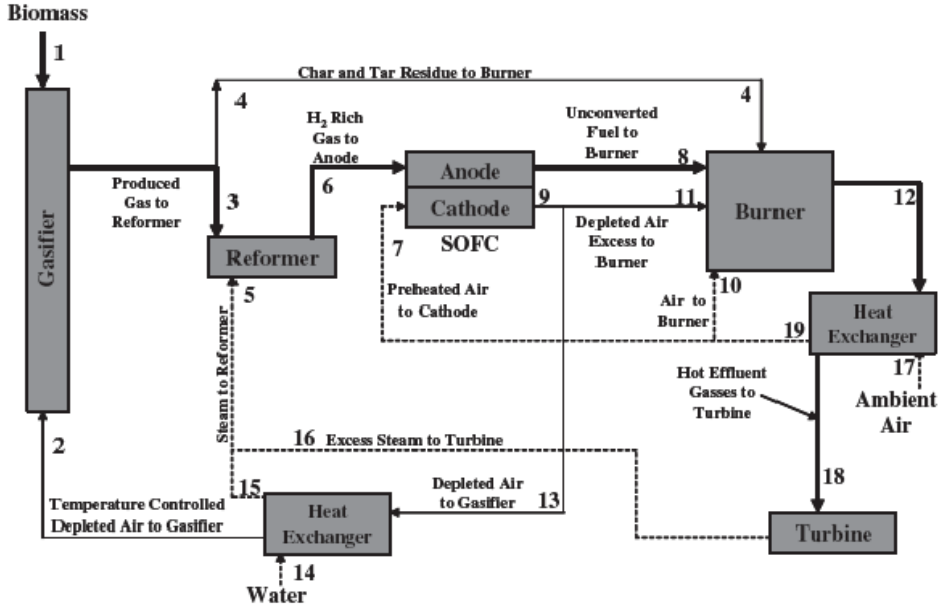

Figure 15. Flow diagram of the gasifier-SOFC integrated process.

The high operating temperature permits SOFCs to run on a range of fuels (natural gas, gasified biomass or coal, anaerobic biogas, etc.), a flexibility which encourages their commercialization opportunities, since pure H_2 is not promptly available. In addition, it gives nominees for high quality heat cogeneration, which can be employed for heating purposes or in thermal engines for additional electric power generation. Power density and fuel utilization decide the overall efficiency of the cell, at the same time that these parameters are readily involved by the operational cell voltage. In the event of the wide range of biogas compositions, the dilution of combustible agent, results in a reduction of the voltage. SOFCs can permit a wide variety of combustible agents, but the operation optimization may require substantial operating condition and system design modifications.

Efficiency of this fuel cell powered generation system with biogas is:

$$\eta_{FC+T} = \frac{P_{FC} + P_T}{\dot{m}_{biomass}\, LHV_{biomass}} \tag{17}$$

where,

P_T electrical power output of turbine (W)

$\dot{m}_{biomass}$ biomass flow (kg/s)

$LHV_{biomass}$ lower heating value of the biomass used (kJ/kg)

Table 5 resumes the lower and higher heating values of several crop residues. The junction of biomass gasification with SOFCs appeared to be a predicting and forthcoming possibility for electricity and heat cogeneration.

Table 5. LHV and HHV of various crop residues (Seitarides *et al*., 2008)

Crop residue	LHV (MJ/Kg)	HHV (MJ/Kg)
Rice husk	—	12.8–14.9
Rice straw	15.3	16.3
Wheat straw	16.5	17.5
Barley straw	18.2—19.4	17.1–18.2
Olive tree prunings	—	18.86
Cotton stalks	—	15.81
Durum wheat straw	—	17.92
Corn stalks	—	17.82
Soft wheat straw	—	17.92
Vineyard prunings	—	16.81
Corn cobs	—	18.02
Sugar beet leaves	—	17.72
Rice straw	—	12.16
Peach tree prunings		18.86
Almond tree prunings		18.43
Oats straw		18.11
Sunflower straw		20.83
Cherry tree prunings		21.78
Apricot tree prunings		20.83

Biogas, regardless of attractive advantages of being indigenous, local, versatile and renewable, while SOFC, owing to their high efficiency, could considerably upgrade the value of this fuel. Running these devices with reformed biogas, looks to be a hopeful way for the production of clean energy from biomass.

6. GAS TURBINE

Since the availableness of compact, reliable, and efficient distributed generation (DG) constitutes user-owned generation a viable economic alternative for industrial and commercial consumers, it has appealed considerable interests in applying them to power distribution system. Microturbine generation (MTG) is a well thought-out type of the DGs (Hatziadoniu *et al.*, 2002; Jurado and Cano, 2004; Traverso *et al.*, 2006).The MTG is principally composed of a gas turbine and a permanent ac generator, put on the same shaft to increase the electrical efficiency. As this shaft moves at the turbine speed, the generator supplies high-frequency ac electricity in the range of several kHz. It needs positing a utility interface power converter behind the generator for changing the electricity to the power frequency (Figure 16).

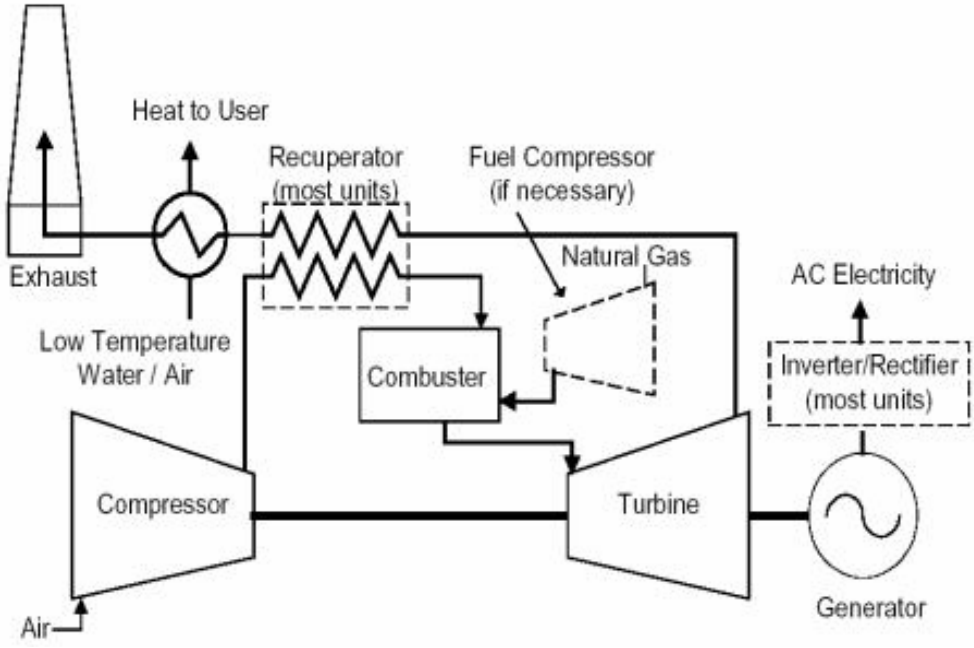

Figure 16. Gas turbine scheme.

Microturbines are a relatively new technology, but they are now commercially available from different manufactures as Capstone, Honeywell, Elliot, Turbec, etc. For example, Table 6 shows technical characteristics of Model 330 manufactured by Capstone.

Table 6. Technical characteristics of the Capstone Microturbine Generator, Model 330

Microturbine Performance (High-pressure and low-pressure natural gas)	
• Full load power	30 kW (HP), 28 kW (LP) at ISO conditions, 59 degrees F, sea level.
• Efficiency (LHV)	27% +/- 2 % (HP), 26% +/- 2% (LP)
• Heat rate (LHV)	12,600 Btu/kWh(HP), 13,000 Btu/kWh(LP)
Emissions (natural gas fuel)	
• NO_x	< 9 ppm / 6.7 g/h / 0.0147 lb/h
Other	
• Noise level	65 dB around 10 meters
• Fuel flow (natural gas - HHV)	410,000 Btu/h / 428,000 kJ/h
• Exhaust gas temperature	520 degrees F / 272 degrees C
• Total exhaust energy	277,000 Btu/hr / 295,000 kJ/h
• Dimensions	74.8" H x 28.1" W x 52.9" D 1900 mm H x 714 mm W x 1344 mm D
• Weight	1052 lbs / 478 kg
• Voltage output	400 – 480 VAC, 3 phase, 3 or 4 wire wyes, underground delta, 43 A max

6.1. Gas Turbine Model

A thorough introduction to gas turbine theory is provided in (Cohen *et al.*, 1998). There also exists a large literature on the modeling of gas turbines. Model complexity varies according to the intended application. Detailed first principles modeling based upon fundamental mass, momentum and energy balances is reported in (Fawke *et al.*, 1972; Jurado *et al.*, 2004).These models describe the spatially distributed nature of the gas flow dynamics by dividing the gas turbine into a number of sections. Throughout each section, the thermodynamic state is assumed to be constant with respect to location, but varying with respect to time. Mathematically, the full partial differential equations model description is reduced to a set of ordinary differential equations, which facilitate easier application within a computer simulation program. For a detailed model, a section might consist of a single compressor or turbine stage. Much simpler models result if the gas turbine is decomposed into just three sections corresponding to the main turbine components, i.e. compressor, combustor and turbine, as in (Hussain and Seifi, 1992).

Instead of applying the fundamental conservation equations, as described above, another modeling approach is to characterize gas turbine performance by utilizing real steady-state engine performance data, as in (Hung, 1991).It is assumed that transient thermodynamic and flow processes are characterized by a continuous progression along the steady-state performance curves. This is known as the quasi-static assumption. The dynamics of the gas turbine, e.g. combustion delay, motor inertia, fuel pump lag, etc. are then represented as

lumped quantities separate from the steady-state performance curves. Very simple models result, if it is further assumed that the gas turbine is operated at all times close to rated speed (Rowen, 1983).

Air at atmospheric pressure enters the gas turbine at the compressor inlet. After compression of the air to achieve the most favorable conditions for combustion, fuel gas is mixed with the air in the combustion chamber. Combustion takes place and the hot exhaust gases are expanded through the turbine to produce mechanical power. In terms of energy conversion, the chemical energy present in the combustion reactants is transferred to the gas stream during combustion. This energy-measured in terms of gas enthalpy-is then converted into mechanical work by expanding the gas through the turbine. Thus, the excess mechanical power available for application elsewhere, after accounting for the power required to drive the compressor, is derived ultimately from the combustion process.

Compressor power consumption equation:

$$P_c = \frac{w_a \Delta h_{IC}}{\eta_c \eta_{trans}} \tag{18}$$

Combustion energy equation:

$$\begin{aligned} & w_g c_{pg} \left(T_{Tin} - 298\right) + w_f \Delta h_{25} + w_a c_{pa} \left(298 - T_{cout}\right) + \\ & + w_{is} c_{ps} \left(298 - T_{is}\right) = 0 \end{aligned} \tag{19}$$

Power delivery equation:

$$P_T = \eta_T w_g \Delta h_{IT} \tag{20}$$

$$P_{mec} = P_T - P_c \tag{21}$$

6.2. Gas Turbine Control Configuration

The concept of the gas turbine control system, which is applied in this paper, is based on the Speedtronic Mark 4 description as presented in (Rowen, 1988).Some considerations concerning the subject may also be found in (Hannett and Khan, 1993; Hannett *et al.*, 1995; Jurado *et al.*, 2002).The simplified gas turbine model is divided into two interconnected subsystems in this chapter. The subsystems are the fuel system (fuel valve with actuator), and the turbine. The fuel flow out from the fuel systems results from the inertia of the fuel system actuator and of the valve positioner.

The fuel system actuator equation is:

$$W_f = \frac{1}{T_2 s + 1} e_1 \tag{22}$$

The valve positioner equation is:

$$e_1 = \frac{a}{bs + c} e_2 \tag{23}$$

Where the input variable to the fuel system is F_d. The output variable from the fuel system model is w_f. A single gas turbine does not require the digital set point feature.

Input variables to the turbine are w_f, $\Delta\omega$ and ω. Output variable from the turbine is P_{mec}. For the purpose of this chapter only modulating control of mechanical side of the gas turbine is of interest. The simplified model of the gas turbine controller in this chapter consists of two inputs and one output. Inputs to the controller are P_{mec} and ω. The output from the controllers is F_d.

Figure 17 represents a SIMULINK block diagram for a microturbine, together with its control and fuel systems. The control system includes speed control, temperature control, and upper and lower fuel limits (Rowen, 1983). The droop governor is a straight proportional speed controller in which the output is proportional to the speed error. The speed governor is the primary means of gas turbine control under part load conditions. The digital set point is the normal means for controlling gas turbine output when operating in parallel and using a droop governor.

As shown in Figure 17, there are two main functions.

Torque function represented in the system allows us to obtain the net mechanical torque. We can express it like:

$$T = k_6 \cdot (W_f - 0.23) + a_1 \cdot (1 - N) \tag{24}$$

where

T	mechanical torque developed by microturbine (p.u.)
N	microturbine rotation speed (p.u.)
k_6 , a_1	coefficients that depend on the LHV of the fuel

The power developed is obtained applying the following equation:

$$P_{MG} = T_m N \tag{25}$$

Temperature function allows to find the instantaneous exhaust temperature of the microturbine´s gases, this is expressed by:

$$T_E = T_{ref} - b_1 (1 - W_f) + b_2 (1 - N) \tag{26}$$

where

T_E	exhaust temperature of the microturbine´s gases (K).

T_{ref} exhaust temperature reference (K).
b_1, b_2 parameters of the ignition temperature.

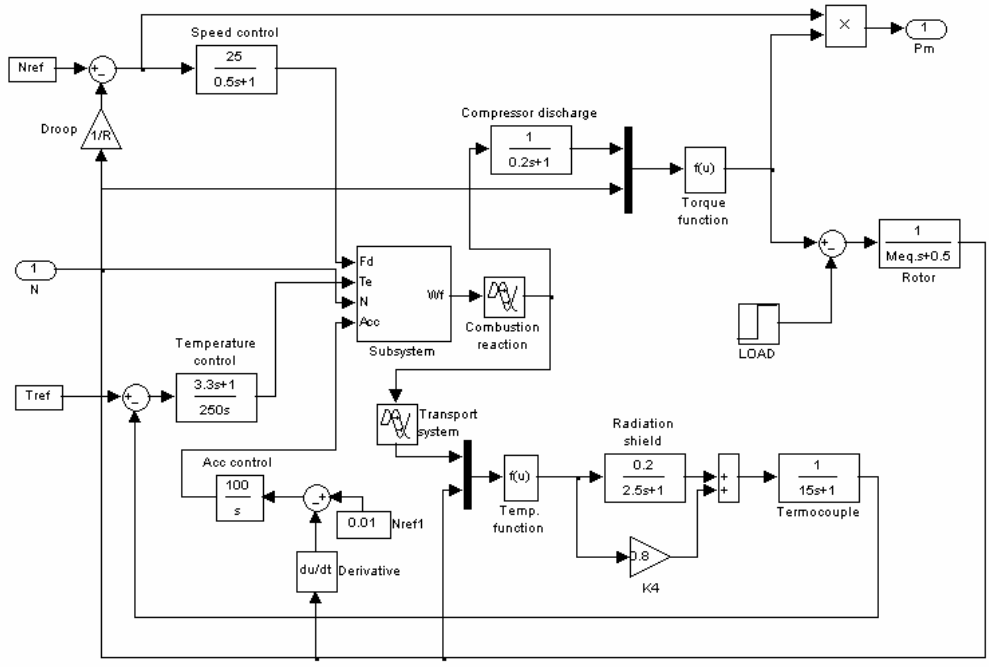

Figure 17. Microturbine Simulink model.

Figure 18 presents the fuel subsystem. The microturbine is essentially non linear. There are small delay times associated with time of the combustion reaction (ECR), volume of compressor discharge and gas transport from the combustion system across the microturbine (ETD).

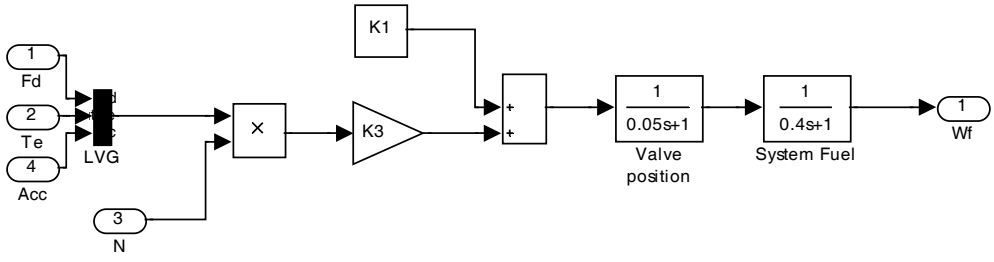

Figure 18. Fuel subsystem.

The parameters used in the simulation are summarized in table 7.

Temperature control is the normal means of limiting gas turbine output at a predetermined firing temperature, independent of the variation in ambient temperature or fuel characteristics. Since exhaust temperature is measured using a series of thermocouples incorporating radiation shields, there is a small transient error due to the time constants associated with the measuring system. Under normal system conditions, where the gas turbine output is determined by the slow rate of the digital set point, these time constants are of no

significance to the load limiting function. However, where increasing gas turbine output is the result of a reduction of system frequency and, therefore, may occur quite rapidly, exhaust temperature measurement system time constants will result in some transient overshoot in the load pickup. The design of the temperature controller is intended to compensate for this transient characteristic.

Table 7. Simulation parameters for microturbine

Speed regulators				
Drop speed	$W = 25$	$X = 0$	$Y = 0,5$	$Z = 1$
Isochronous	$W = 30$	$X = 2,5$	$Y = 0,1$	$Z = 0$
Temp. and accelerat.	$T_5 = 3,3$ s		$T_T = 250$ ºC	$K_{acc} = 100$
Fuel system characteristics				
$a = 1$	$b = 0,05$		$c = 1$	$K_6 = 1,3$
$K_1 = 0,23$	$K_2 = 0$		$K_3 = 0,77$	$T_2 = 0,4$
Microturbine characteristics				
$E_{CR} = 0,01$	$E_{TD} = 0,04$		$T_{cd} = 0,2$	
$a_1 = 0,5$	$b_1 = 390$		$b_2 = 306$	$T_{ref} = 510$ ºC
Temperature gauges (thermocouple)				
$K_4 = 0,8$	$K_5 = 0,2$		$T_4 = 15$	$T_3 = 2,5$
Rotor control	characteristics		LVG	
Me = 0,7	*D = 0,5*		*MAX=1,5*	*MIN = -0,1*

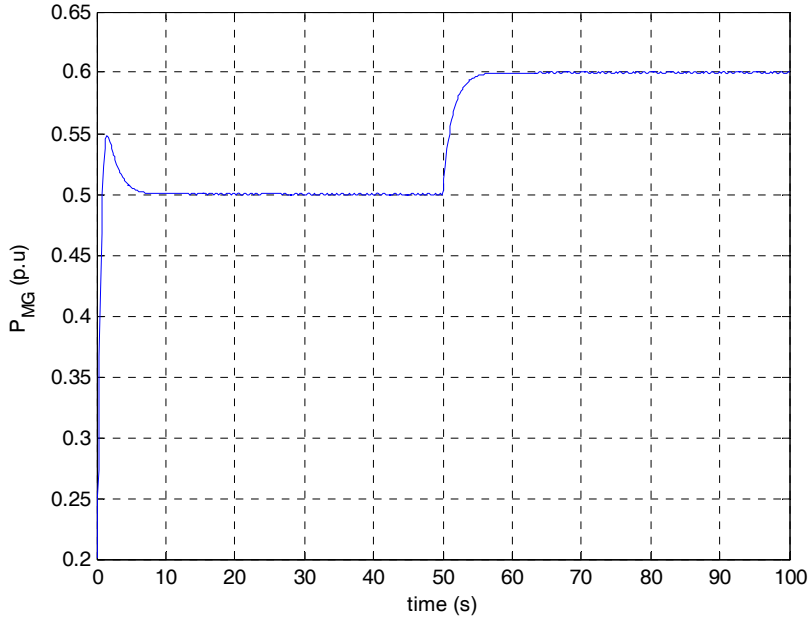

Figure 19. Microturbine mechanic power (p.u.).

It can been observed in Figure 19 as the mechanical power delivered by microturbine matches perfectly to the step load. There exists an initial power peak due to overcurrents in

the transitory period. Microturbine response time is much more rapid than that in fuel cell (350-400 s), since the mechanic power becomes stable at about 10 s.

The P_{mec} is regulated solely by the fuel mass flow. As more fuel enters the combustion chamber, more heat is generated, and more power is produced in mechanical form. A step change in the fuel valve position will not result in an instantaneous increase of power. Actually, at the time of the change, the output power decreases. The speed of the turbine had not had time to change, and consequently, the air flow entering the combustion chamber did not have time to increase. The increased fuel rate generates a non-ideal stoichiometric ratio between the fuel and air, instantaneously lowering the power available at the shaft. As the turbine-compressor block increases speed, more air is drawn into the combustion chamber, allowing for all the extra fuel to be burned and, in turn, for a higher power output.

6.3. Biomass and Gas Turbine

Figure 20 displays the simplified outline of the small scale (100 kWe), biomass fuelled microturbine power plants considered. Afterward drying, the biomass flows the biomass furnace (BF) together with the hot air exiting from the turbine (T). The high temperature gases developed by the biomass furnace are cooled in the high temperature heat exchanger (HTHE) by heating the compressed air up to the demanded turbine inlet temperature (TIT). The exhaust waste heat is retrieved in the rotary dryer (RD) by drying the raw biomass. Differently, the exhaust heat can be retrieved through a low temperature heat exchanger (LTHE). A by-pass valve (BV) has been also added to adjust the air mass flow.

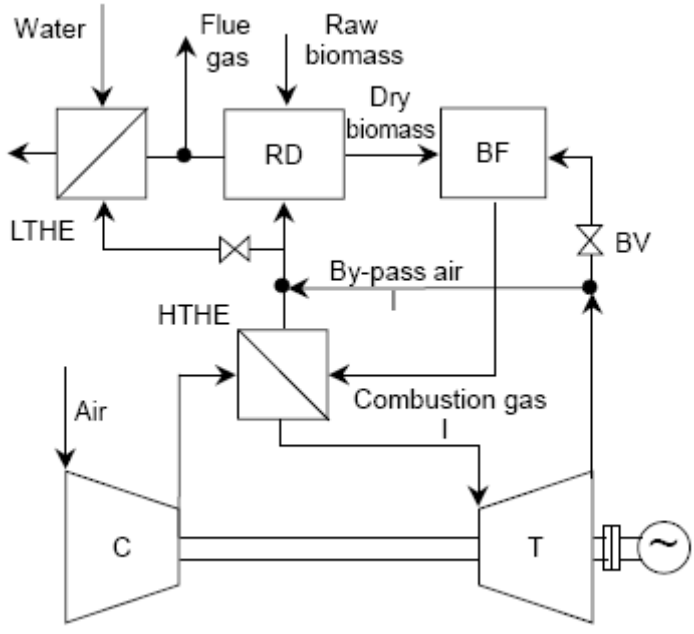

Figure 20. Scheme of microturbine power plant integrated with biomass.

When biomass is gasified, relatively large quantities of tar are produced, e.g. from 10% of the fuel in an updraft gasifier to 2-4% in a fluidized bed. The amount and composition of the tars are dependent on the fuel, the pyrolysis conditions and the secondary gas phase reactions.

If the tar is allowed to condense when the gas is cooled (condensation temperature of tar from woody biomass is 200-500ºC) considerable problems with equipment contamination (such as filter clogging) result. Fuel nitrogen is largely converted to ammonia, which on firing of the gas will form nitrogen oxides. Apart from tars, gas turbines require a minimum LHV of the gas and are sensitive to dust. In addition, alkali compounds are detrimental to gas turbines, causing corrosion and deposits at the high working temperatures of turbines.

The requirement for a higher gas pressure has led to the development of two distinct schemes for integrating the gasification system to the gas turbine; pressurized gasification: hot gas filtering and cleaning, and atmospheric gasification: cold gas filtering and cleaning.

A variety of relatively large-scale biomass gasification technologies are at various advanced stages of development. Three gasifier/gas cleanup designs are considered here: (i) atmospheric-pressure air-blown fluidized-bed gasification with wet scrubbing [31], its higher heating value (HHV) is 6.47 MJ/kg, $\%H_2 = 16.6$, and $\%CH_4 = 3.4$; (ii) pressurized air-blown fluidized-bed gasification with hot-gas cleanup (Salo *et al.*, 1998), the HHV is 5.48 MJ/kg, $\%H_2 = 15.5$, and $\%CH_4 = 0.05$; (iii) atmospheric-pressure indirectly-heated gasification with wet scrubbing (Paisley and Anson, 1997), the HHV is 18.1 MJ/kg, $\%H_2 = 29.5$, and $\%CH_4 = 13.05$. Gumz is the earliest reference found describing the concept of combining a pressurized gasifier with a gas turbine engine (Gumz, 1950).

7. FUEL CELL AND GAS TURBINE HYBRID SYSTEM

SOFCs integrated with gas turbines of small size (less than 1 MW) are attracting wide interest (Roberts *et al.*, 2006) as these systems are able to simultaneously solve some of the key problems of small gas turbines (low efficiency and NO_x emissions due to the combustor) and of SOFCs. The pressurized SOFC module substitutes the combustor of the regenerated turbine plant, and the clean effluent has a temperature of about 900°C, which well matches the requirements on the inlet temperature of first generation microturbines.

In (Roberts *et al.*, 2006) the impact of the gas turbine rotational speed on dynamic performance and controllability of a hybrid system is investigated. The transient response of the hybrid system to perturbations in the power demand is investigated. Kaneko *et al.* treat how the power and temperature are controlled in a biomass gas fueled SOFC and microturbine hybrid system. A SOFC and MGT dynamic model is developed and used to simulate the hybrid system performance operating on biogas (Kaneko *et al.*, 2006).

The evaluation of SOFC combined heat and power system configurations for application in residential dwellings is explored through modeling and simulation of cell stacks including the balance-of-plant equipment (Braun *et al.*, 2006). In (Wachter *et al.*, 2006) a nonlinear model with bulk parameters and dynamic states is presented.

Solid State Energy Conversion Alliance (SECA) is the U.S.'s major national stationary fuel cell program and the main thrust of the DOE FE DG Fuel Cell Program. SECA is also recognized as part of the FutureGen and Hydrogen Programs (Williams *et al.*, 2006).General

Electric is evaluating several stack designs and is especially interested in extending planar SOFC's to large hybrid systems.

The fuel cell-turbine hybrid is a key part of the FutureGen plant to produce hydrogen from coal. The highly efficient SOFC hybrid plant, with its SECA fuel cells, will produce low-cost electric power and other parts of the plant could produce hydrogen and sequester CO2. The hydrogen produced can be used in fuel cell cars and for SOFC DG applications.

For several applications, such as in electric power generation, the SOFC is expected to be one of the most promising future power sources because of its high efficiency and low emission. It has been theoretically proven that a SOFC-based hybrid power system combined with a gas turbine might provide higher efficiency than the SOFC alone (Massardo and Lubelli, 2000; Chan *et al.*, 2002). Despite various proposals for system configurations and prototype tests during the last several years, SOFC/GT hybrid systems have only been developed for kW-class power generations (Veyo *et al.*, 2002; Veyo *et al.*, 2002; Litzinger *et al.*, 2005).

Siemens-Westinghouse Power Corporation developed the first advanced power system, which integrates a SOFC stack with the gas turbine engine. The pressurized (3 atm) system generates 220 kW of electrical power at a net electrical efficiency of 55% (U.S. Department of Energy, 2004). Figure 21 presents a photograph of the first SOFC/GT system in the world (Hamilton, 1999).

Nevertheless, as pointed in the Vision 21 Technology Roadmap announced by the Department of Energy, USA, 1999, a SOFC-GT hybrid system will finally be developed for commercial entry into multi-MW distributed generation applications.

To apply a SOFC-GT hybrid system to large power generations, the amount of power generated by both the SOFC and gas turbine must be modified. Usually, increasing the number of unit cells and/or substack modules can raise the SOFC power. With the exception of its size, there are no outstanding changes in the SOFC configuration with an increased generated power. However, the configurations and operating characteristics of gas turbines vary greatly with generated power.

Figure 21. Schematic diagram of a 220 kWe SOFC/GT system.

7.1. Configuration of the SOFC-GT Plant

The coupling of high temperature fuel cells with gas turbines is by no means new, and has been discussed for several years. Recent technical papers have covered a wide range of topics, these includes the following: (1) systems involving midsized and large gas turbines (Veyo and Lundberg, 1999); (2) dynamic modeling, performance, technical issues, and integration considerations (Liese, 1999);(3) microturbine specific studies (Campanari, 1999); (4) details of experimental programs to demonstrate the coupling of a microturbine with a solid-oxide fuel cell SOFC (Leeper, 1999).

When used in combination with turbines, fuel cells can produce from 55 to 90% of the electricity of the system while turbines produce the remainder. Several cycle configurations have been proposed and the terminology is still evolving, but one useful way of looking at the differences is to divide the configurations into those that include 'directly fired turbines' and those with 'indirectly fired turbines'.

A hybrid power system with a directly fired turbine normally uses a pressurized fuel cell to provide input to the turbine, thus acting as a combustor. In the indirectly fired turbine system, an atmospheric fuel cell is used and a pressurized heat exchanger provides input to the turbine. When utilizing the fuel cell/gas turbine combination the combined efficiency of the system is raised to greater than 60% and criteria pollutant emissions are essentially eliminated. An example of a hybrid system with an indirectly fired turbine is shown in Fig. 22.

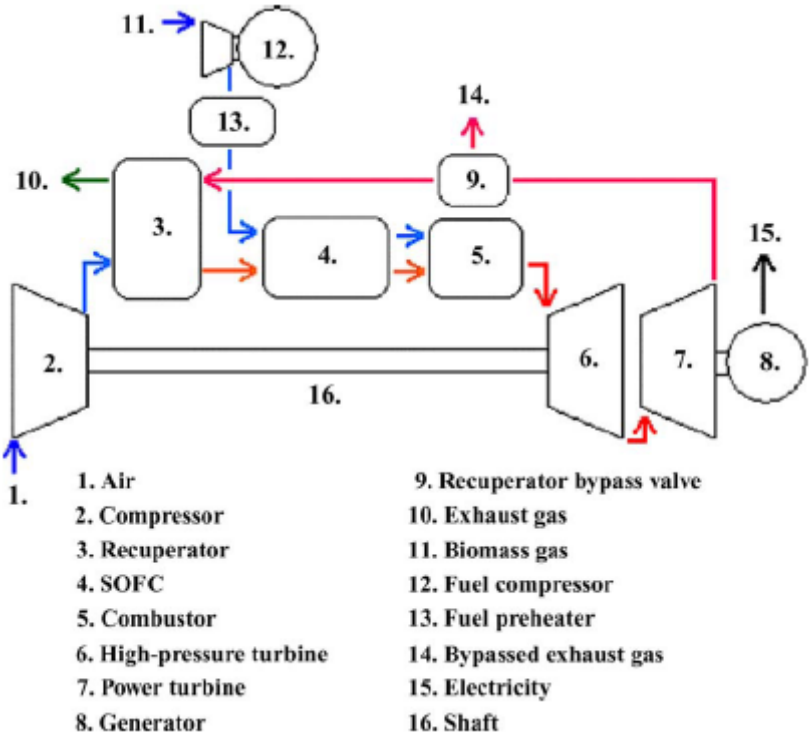

Figure 22. Schematic of SOFC-microturbine hybrid system.

The hybrid system described in this chapter consists of a compressor, recuperator, SOFC, combustor, two turbines, and a bypass valve. The SOFC is used as a topping cycle, that is, it operates under the pressurized conditions between the compressor and first turbine of the MGT. One turbine is directly connected by a shaft to drive the compressor and the other turbine is connected to an electric generator. The biomass gas fueled is pressurized and preheated before entering the SOFC to avoid excess cooling and thermal stress in the fuel cell stack. A bypass valve is for controlling the portion of exhaust gas flow goes into recuperator.

In the fuel cell/turbine hybrid power plant, the fuel cell does not need to operate at the turbine pressure, instead it operates at the preferred ambient pressure and it's independent of gas turbine cycle pressure ratio. The system works efficiently with a wide range of turbine compression ratio. This allows taking a system developed for integration at the multi-MW scale with industrial size turbines, and configuring a small MW class system using a microturbine at a lower pressure ratio.

CONCLUSION

Biomass gasification is a possible technology for producing low-medium calorific gas from biomass. High gasification temperature leads to more hydrogen production, but diminishes also the gas-heating value.

The concurrence of biomass gasification with SOFCs and microturbines appeared to be a hopeful and forthcoming possibility for electricity and heat cogeneration along with sound environmental and socioeconomic profits.

The conjunction of SOFCs and microturbines with gasifiers can lead significantly to defeat the endothermicity of the latest and avoid the capital costs of the biogas-reforming stage. The quality of SOFCs system to hold the anode and cathode exhaust gases separate permits the development of SOFC over-fueling and lending downstream functions for the anode exhaust gases, such as a gas turbine.

The cause for using biofuels in SOFCs and microturbines is considered to be both environmental and financial, because connection to the grid can be costly in such areas where biogas can be obtained on site with no substantial extra costs. Regardless of the benefits of fuel cells, their potential to become a feasible option depends on the capital cost of the system. Fuel cells require to be cost-competitive compared to conventional generation systems.

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Chapter 7

ALLOTHERMAL GASIFICATION: REVIEW OF RECENT DEVELOPMENTS

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ABSTRACT

In recent years, allothermal gasification has been receiving increased attention and a number of systems exploiting its advantages have been proposed or are under development. Allothermal gasifiers can offer a number of significant advantages over their more wide-spread counterparts, the autothermal gasifiers, especially for biomass gasification.

The main drawback of autothermal gasification, which generates heat in-situ by partial combustion of its feedstock, is the dilution of the product gas by products of combustion and inert gases (e.g., N_2) introduced in the oxidizer stream (e.g., air). As a result, air gasification yields a product gas with only low calorific value. To obtain high calorific product gas, pure oxygen is often used in autothermal gasification instead of air, as the oxidizer. This however, requires installation of air separation units, which results in higher construction and operation costs, plus efficiency penalty. Allothermal gasification, on the other hand, relies on the use of external heat sources to drive the endothermic gasification reactions within the gasifier. This physical separation of heat generation and gasification brings about the main benefits of allothermal gasification, i.e., absence of diluting gases from partial combustion of fuel feedstock within the gasifier and subsequent higher calorific value of the product gas.

However, the reliance of allothermal gasification on external heat supply also presents one of its main challenges, i.e., the effective transfer of heat between the heat source and the gasification chamber. Some systems use solid heat carriers circulating between two separate reactors while other systems rely on heat exchangers (e.g., heat pipes). The most suitable way for a particular gasifier configuration depends on both the heat source and the gasifier type.

The main aim of this chapter is to present a comprehensive overview of the state of the art in the field of allothermal biomass gasification. This chapter will introduce the

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field of allothermal gasification by presenting the different forms it can take, their main features and advantages. It will review recent developments in the area and highlight its successes.

1. INTRODUCTION

The great risks related to the uncontrolled release of greenhouse gases, especially CO_2, to the atmosphere, have been widely recognized and score high on the agenda of most governments [1-3]. Carbon dioxide, as the inevitable product of all energy conversion processes based on carbonaceous resources, has become one of the hottest topics of the past decade. Until today, national governments of 166 countries ratified the Kyoto Protocol in an attempt to curb global emissions of greenhouse gases (GHG) of which the CO_2 is by far the most abundant one. However, this task is by no means going to be easy, as reducing the GHG production must not cause serious damage to the economies of participating countries, therefore should not hamper economic growth.

The urgent need to reduce the CO_2 emissions is applying further pressure on the efficiency of new systems and is driving the search for alternative fuels, which are becoming competitive due to high oil prices and rising coal prices. Increasing amounts of biomass, in various forms ranging from dedicated energy plants to waste materials, are expected to be used to substitute fossil fuels, where possible. This is because biomass, unlike other carbonaceous fuels is a renewable resource available in different forms worldwide. Its main advantage as a substitute fuel is the fact, that it can be carbon neutral and therefore does not contribute to the global warming; hence, CO_2 sequestration might not be necessary for processes using biomass, and if deployed, it would make the use of biomass carbon negative.

New conversion technologies are being developed and introduced, aiming for higher efficiency in converting the stored chemical energy into electricity, heat and other valuable byproducts. The present state of the art systems are referred to as combined cycle systems [4, 5], because they combine more than one thermodynamic cycle, typically Bryton cycle (combustion turbine) and Rankin cycle (steam turbine), thus reaching significantly higher efficiency than conventional steam cycles alone. However, as the key component of a combined cycle is combustion turbine (CT), it only accepts gaseous or alternatively liquid fuels.

To enable the use of solid fuels such as coal or biomass in the combined cycle system, it is necessary to convert them into gas. The resulting system is then referred to as integrated gasification combined cycle (IGCC) [6] and its main feature is the presence of gasifier, in which solid fuel is converted into fuel gas that is later combusted in the CT. Such system successfully combines the advantages of combined cycle, i.e., high efficiency, with the ability to utilize solid fuels. Moreover, the product gas from the gasifier can be used not only to fuel the CT, but the hydrogen separated from the product gas can serve as fuel for fuel cells; hence, further increasing system efficiency. Alternatively, part of the gasification products can be used for production of chemicals and liquid fuels.

In general, gasifiers can be divided into two categories, the more widespread autothermal gasifiers and the allothermal gasifiers. Autothermal gasifiers use either air or oxygen to combust part of the feedstock within the gasification chamber, to drive the endothermic gasification reactions. Allothermal gasifiers on the other hand rely on external heat supply

and therefore do not require the use of air or oxygen for their operation, Instead, pure steam is used as a gasification medium. As steam can be easily removed from the product gas by condensation, the remaining gas contains very high concentration of H_2 and is thus suitable for a number of applications (e.g., fuel cells).

The concept of allothermal gasification is by no means new. It has been around in various forms for over 30 years. The earliest designs focused on the use of heat available from nuclear reactors [7] and aimed at gasification of coal. Later designs focused on the use of heat generated by the combustion of gasification residues, in separate reactor. Probably the first allothermal gasifier for biomass was designed and built in the mid-70's in Japan [8], for the gasification of refuse derived fuels (RDFs). Since then, number of different systems has been developed and several technologies reached demonstration stage. Despite the considerable differences between the various designs, all these processes have one thing in common; they all use pure steam to gasify their feedstock. The use of pure steam, as compared to air has the advantage of producing syngas with very high concentration of H_2, due to the absence of diluting gases such as N_2. Its comparative advantage to gasification using O_2 lies in the fact that costly air separation system for production of pure O_2 is not required.

Despite all these advantages, allothermal gasification is considerably less widespread than autothermal gasification. The main reason for the relatively low market penetration of allothermal gasifiers is the fact that the use of pure steam as a gasification media is very energy intensive. The large volumes of steam at very high temperature, required in the gasification zone, together with low efficiency of its use, less than 10%, lead to significant demand on heat input. This heat is supplied from external sources and is either in the form of waste heat from industrial processes or as heat generated by combustion of gasification residues, such as char and tar. It is the transfer of heat into the gasification reactor that presents the single biggest challenge for allothermal gasification. And it is the means of heat transfer that distinguishes between the different processes developed to date.

This chapter will review the development and deployment of allothermal gasification technology in the past decade. For the purpose of this chapter, the allothermal gasification systems will be classified into two categories, based on the means of heat transfer into the gasification zone. The first category includes systems, using solid heat carriers circulating between different reactors, while the second category consists of those relying on heat exchangers. There has been a large number of allothermal gasification systems proposed and developed, however, this chapter will focus only on those that have reached the pilot-scale stage, or even commercial deployment.

2. SYSTEMS BASED ON CIRCULATION OF SOLID HEAT CARRIERS

This category of gasifiers comprises of systems that use solid particles to transfer heat between the combustion zone (at higher temperature) and the gasification zone (at lower temperature). This type of allothermal gasifiers has been so far the most successful with a number of pilot-scale demonstration plants. Some of these systems deploy two fluidized-bed reactors and are therefore usually referred to as Dual Fluidized-Bed (DFB) gasifiers. Corella et al. [9] recently published a review of the past and ongoing research in this field and therefore only most important issues, related to the DFB systems, and especially their

deployment, will be discussed in this chapter. In addition to the DFB gasifiers, systems with other means of solids transfer have been developed and successfully deployed, and will be presented here. Following is the list of systems that belong to this category:

- Battelle/FERCO gasifier
- Fast Internally Circulating Fluidized Bed (FICFB) gasifier
- Staged reforming - Blue tower
- MILENA gasifier

2.1. Battelle/FERCO Gasifier

The Battelle/FERCO gasification process [10] is based on the technology developed in the eighties by Battelle – Columbus Laboratories [11] and was successfully tested in a pilot plant at the McNeil power station in Burlington, Vermont [12]. This system produces medium heating value product gas (about $16.9\,\mathrm{MJ.m_N^{-3}}$) at atmospheric pressure and without oxygen supply. The typical composition of the product gas from the pilot plant is: H_2 22 vol.%, CO 44.4 vol.%, CO_2 12.2 vol.%, CH_4 15.6 vol.%, C_2H_6 0.7 vol.% and C_2H_4 5.1 vol.% [13]. The Battelle/FERCO process is schematically shown in Figure 1. The system consists of two physically separated circulating fluidized bed (CFB) reactors: (a) the gasification reactor and (b) the combustor. In the gasification reactor, the feedstock is converted into medium heating value product gas and char in presence of steam and hot solid heat carrier coming from the combustor.

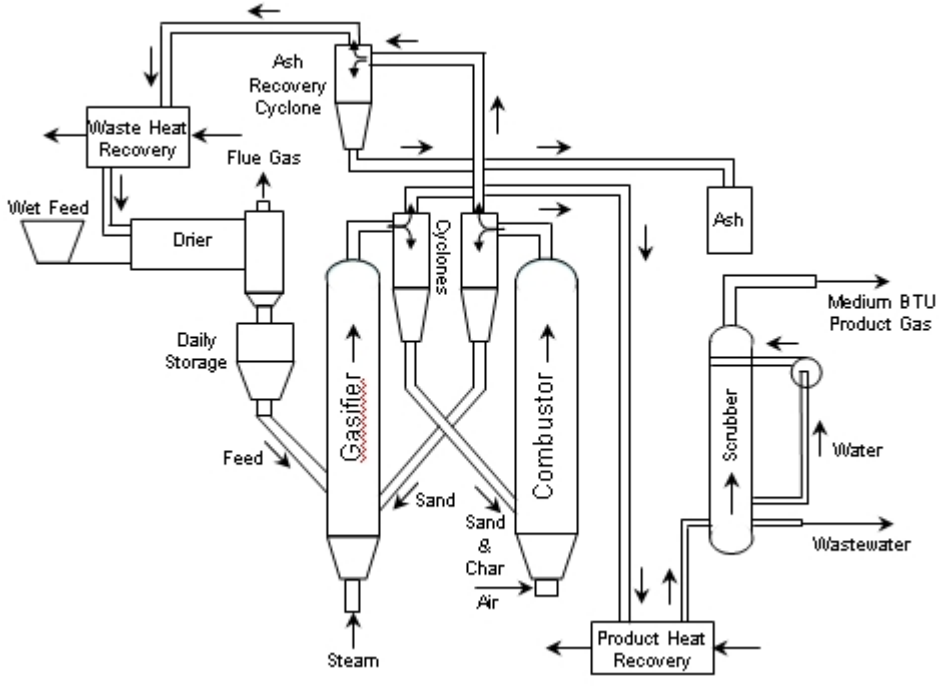

Figure 1. The Battelle/FERCO gasification system.

The gasification temperature ranges from 650 – 1000°C. The solids, i.e., the char and the heat carrier, are separated from the product gas in the cyclone and transferred to the combustor. The product gas is then cleaned in a scrubber and the collected tar is introduced to the combustor. In the combustor, the solid heat carrier is reheated by the combustion of char and tar in air and then returned to the gasification reactor. The Battelle/FERCO process, takes advantage of the very high reactivity of biomass that allows throughputs as high as 14.6 $t.h^{-1}.m^{-2}$. The process had been demonstrated on a nearly commercial scale (42 MW_{th}), in Burlington, as a part of existing wood-fired power plant. Extensive experimental testing had been carried out between 1997 and 2002. The first operation in full steam gasification mode was achieved in August 1999 after necessary improvements on the gasifier auxiliary systems (e.g., feeding, solids separation, gas processing). The system showed high availability during extended operating periods and also high flexibility regarding the feedstock type, ash content and moisture content. Based on the information available in the public domain, it can be concluded, that after resolving the initial problems with feeding and gas processing, the overall performance of the system was good and that the technical viability of the system had been successfully demonstrated. However, in 2002, after completion of the test program supported by the DOE, the gasification facility was decommissioned, and to authors' knowledge, at present there is no operating facility based on this technology.

The Battelle/FERCO technology is being marketed by SilvaGas Corporation, the successor of FERCO. Recently there have been two commercial plants under consideration; one plant in the UK, the so called Winkleigh Biomass Project (Winbeg) [14] and one in the USA, the so called Tallahassee Renewable Energy Center [15]. The Winkleigh Biomass Project aimed at construction of a 23 MW_{el} power plant based on the Battelle/FERCO technology [16] and in 2003 was awarded a grant from the UK Department of Trade and Industry (DTI). However, the project never took off as the developer failed to secure a planning permission, which was followed by a withdrawal of the government grant in 2006 [17]. The most recent commercialization effort is the Tallahassee Renewable Energy Center in Florida (USA). The plant is projected to use approximately 730 ton of biomass per day (on dry basis), generating 42 MW of electricity and 63.3 GJ of methanated gas for the city's pipeline. The construction of the plant is scheduled to commence in early 2009, with the start of operation at the beginning of 2011.

2.2. Fast Internally Circulating Fluidized Bed (FICFB) Gasifier

The FICFB technology had been developed at the Technical University of Vienna in co-operation with AE Energietechnik. It is similar in principle to the FERCO/SilvaGas process as it uses sand as a heat-carrier bed material. However, the FICFB process relies on closely coupled fluidized beds, thus achieving compact design and low heat losses. The initial development work had been undertaken on a cold flow model and a small scale rig (10 kW_{th}). Data from these experiments were than used to design and build the first pilot plant (100 kW_{th}). This pilot plant had been used from early 1995 to late 1999 when a new pilot plant of same basic design and capacity, but with improved operational performance, was installed. The new pilot plant has been used for optimization of the operating conditions (e.g., temperature, steam/fuel ratio). In late 2000 a new 500 kW_{th} gasifier was commissioned and after initial problems started operation in January 2001. This facility had been used for

development and testing of new fluidized bed catalyst that would reduce tar content in the product gas and increase the yield of hydrogen. In addition, the rig served for generation of data necessary for further scale-up. This research and development efforts culminated in a design and construction of a CHP plant based on the FICFB technology in Güssing (Austria) [18, 19], which commenced operation in 2002. The design parameters of the CHP plant are shown in table 1.

The plant has been in operation since 2002 and has been continuously developed, to accommodate for testing of various advanced biomass conversion technologies. In the core of the Güssing biomass CHP stands the FICFB gasifier, as shown in Figure 2.

The feedstock (wood chips) is supplied from a daily hopper via a metering bin to a screw feeder that feeds it into the fluidized bed reactor. The reactor consists of two zones: (a) a gasification zone and (b) a combustion zone. The gasification zone is a bubbling fluidized bed where the biomass is converted to gas and solid residues, in pure steam atmosphere at temperatures between 850 and 900 °C. The steam used for fluidization of the gasification section is generated by the residual process heat.

Table 1. Design parameters of the FICFB-based CHP plant in Güssing (Austria)

feeding rate (wood chips)	[t/h]	2.2
fuel moisture content	[wt.%]	15-35
thermal input	MW	8
electrical output	MW	2
thermal output	MW	4.5
electrical efficiency	%	25
total efficiency	%	80

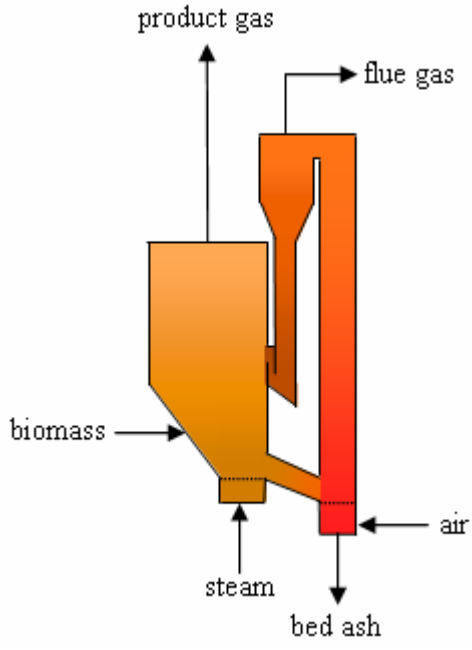

Figure 2. The FICFB gasifier.

The combustion zone is a circulating fluidized bed reactor that provides the heat needed for the endothermic gasification process by burning solid gasification residues (i.e., char) and tar with air. The heat from the combustion zone is transferred to the gasification zone by the circulating bed material. The sensible heat in the flue gas from the combustion zone is used for superheating steam, district heating and preheating of air.

The gas produced in the gasification section is cooled and cleaned in two stages. First, the temperature of the gas is reduced from about 850 °C to approximately 140 °C by a water cooled heat exchanger. In the next step, the particles and some tar is removed from the product gas by a fabric filter. These particles and tar are fed to the combustion zone. In the final clean-up step, the remaining tar is removed from the gas in a scrubber. The spent scrubber liquid saturated with tar is vaporized and fed into the combustion zone for thermal disposal. The temperature of the product gas, after the scrubber, is approximately 40 °C, which is the temperature required for its use in an gas engine. The resulting product gas is then combusted in the gas engine for electricity and heat generation. Alternatively, the product gas can be burned in the boiler for heat generation. The sensible heat from the engine's flue gas is used for district heating. Since its start in 2002, the CHP plant has been in operation for more than 33 000 hours, supplying the town of Güssing with heat and electricity.

In addition to the CHP, there are pilot plants in operation at the Güssing plant that produce substitute natural gas (SNG) and liquid fuels from the product gas [20, 21]. One of the most recent developments in the FICFB technology is the incorporation of so called Absorption Enhanced Reforming (AER) process. The principle of this process lies in the use of active bed material (e.g., lime) that absorbs CO_2 in the gasification zone and releases it in the combustion zone. The process of repeated absorption and release of CO_2 by lime is called the calcination-carbonation process [22] and can be described by the following equations. The eq.1 describes the absorption of CO_2 (i.e., carbonation) and the eq.2 describes the desorption of CO_2 (i.e., the calcination).

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \text{(eq.1)}$$

$$CaCO_3 \rightarrow CO_2 + CaO \qquad \text{(eq.2)}$$

The in-situ removal of CO_2 from the gasification zone shifts the equilibrium of reaction 3, promoting the forward reaction and increasing the yield of hydrogen.

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad \text{(eq.3)}$$

The operational experience from the Güssing plant shows promising results, with H_2 concentrations as high as 74 vol.% [23]. The product gas composition is shown in table 2, together with gas composition from conventional gasification (without AER). It can be seen, that beside the significant increase in H_2 concentration and subsequent decrease in CO and CO_2 concentration, the yield of tar decreased dramatically in the case of AER. In addition, due to the considerably lower gasification temperature, the tar composition shifted towards lighter compounds.

Table 2. comparison of product gas composition from conventional gasification and AER at the Güssing CHP plant

	unit	Conventional (Olivine)	AER
H_2	[vol. % (db)]	35-45	66-74
CO	[vol. % (db)]	22-25	5-8
CO_2	[vol. % (db)]	20-23	6-8
CH_4	[vol. % (db)]	9-11	7-9
C_2H_4	[vol. % (db)]	2-3	1.1
H_2/CO	[-]	1.6-1.8	8-10
Gravimetric tar GCMS tar	[g/Nm^3] [g/Nm^3]	5.8 16.4	0.4 3.9

The long term successful operation of the Güssing CHP plant, demonstrated that the FICFB technology is a viable option with good potential for replication. In fact, there are already plans for construction of a 10 MW_{th} plant in Baden-Württemberg, Germany [24].

2.3. Staged Gasifier – The Blue Tower

The staged gasification process [20] has been initially developed by a German company DM2, and is also known as the "Blue tower" [25 - 27]. This technology is considerably different from the two previously described systems, the Battelle/FERCO and the FICFB, even though, it also relies on the use of solid heat carrier to transfer heat between different zones of the system. However, unlike the other two systems that use two zones, i.e. the gasification and the combustion zone, the staged gasification process uses four different conversion zones. In addition, it also uses different means of circulation of the solid heat carrier. Instead of relying on interconnected fluidized beds with complex systems for material circulation, the staged reforming process uses mechanical transport of the heat carrier.

The process flow sheet is shown in Figure 4, and depicts the four main components of the staged reforming process; the pyrolyzer, the reformer, the combustor and the heat carrier preheater. In the first stage, the biomass is pyrolyzed, forming volatiles and char. The char is transferred to the combustor and burned, releasing heat, while the pyrolyzis gas, containing volatiles rises to the reformer. The gas climbs up to the reformer counter-current to the heat carrier, which is flowing from the reformer to the pyrolyzer. In the reformer, the organic species in the pyrolyzis gas are cracked and reformed to H_2 and CO in the presence of steam. The heat needed in both the pyrolyzer and the reformer to drive the endothermic reactions is supplied by the solid heat carrier. The heat carrier is in form of metal or ceramic spheres that are heated to about 1000 °C, in the solid heat carrier preheater, by the flue gas from char combustion. The heat carrier releases its energy first in the reformer, maintaining it at temperature of about 950 °C, and then in the pyrolyzer, at temperature of aboout 550 °C. After releasing its heat in the pyrolyzer, the heat carrier is mechanically transferred (lifted) back to the preheater.

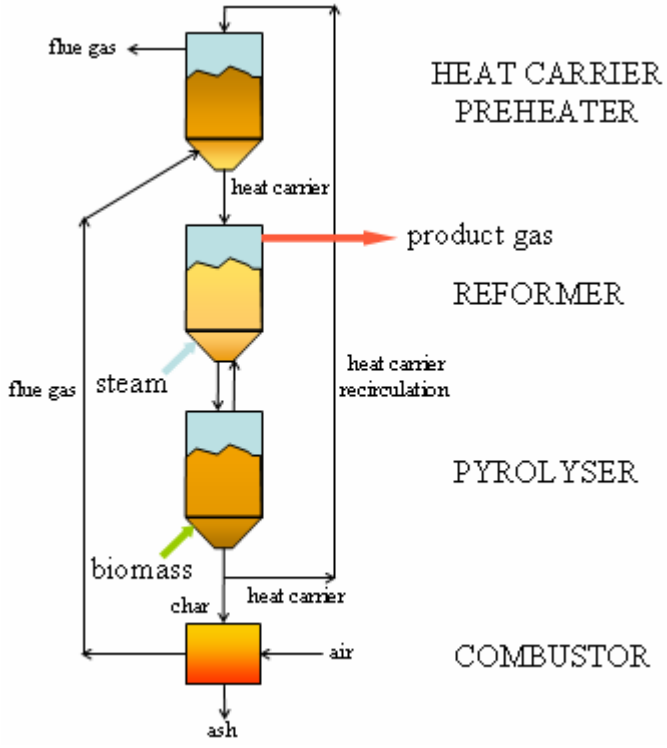

Figure 4. The staged reforming (Blue Tower) process schematic.

This system has been first demonstrated in a 1 MW_{th} pilot plant erected in Herten, Germany, in 2001. It was designed to use feedstock of up to 30% moisture content and sizes up to 50 mm [28]. The resulting product gas has a medium heating value (13 MJ/Nm^3) and a high concentration of H_2 [29], as can be seen in table 3.

The staged reforming technology is being marketed under the name "Blue Tower" by two companies; Eco-Alchemy Inc. (AEI) and Full Market Media (FMM) [30]. Until today, this technology has achieved relatively wide deployment, with one demonstration plant in Germany (Herten), two operating demonstration plants in Japan (in cities of Anan and Izumo) and one commercial plant currently under construction also in Japan [31].

Additional licenses were sold also to other countries around the world. One reason for this relatively fast and successful replication of this technology can be the fact that due to its compact nature, fuel flexibility and ease of operation, it is well suited for small scale plants that can take advantage of locally available biomass and bio-waste, requiring relatively low investments.

Table 3. Composition of the product gas from the staged reforming process pilot plant at Herten, Germany

H_2	CO	CO_2	CH_4	C_2-C_3	N_2	unit
53	12	25	6	2	2	[vol.% (d.b.)]

2.4. MILENA Gasifier

MILENA is a gasification technology developed at the ECN in Netherlands [32], with the aim to design a high efficiency system for generation of substitute natural gas (SNG) from biomass [33, 34]. The principle of operation is very similar to the Batelle/FERCO and the FICFB gasifier concepts, however, with even closer integration of the gasification and combustion zone, thus resulting in simpler, more compact design that is better suited for operation at elevated pressure.

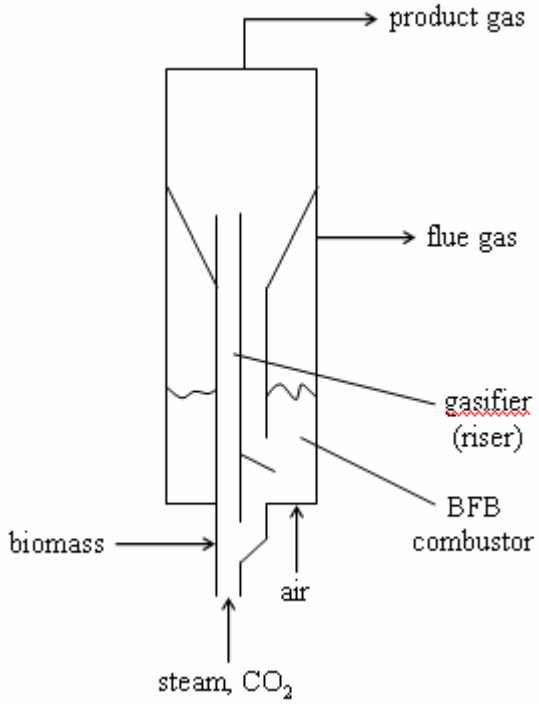

Figure 5. Schematics of the MILENA gasifier.

Table 4. composition of the product gas and the flue gas from the laboratory scale MILENA gasifier

	unit	product gas	flue gas
H_2	[vol. % (db)]	18	
CO/CO_2	[vol. % (db)] [vol. % (db)]	44/11	15
N_2 + Ar	[vol. % (db)]	4	71
CH_4	[vol. % (db)]	15	
C_2-C_5	[vol. % (db)]	6	
C_6-C_7 tar (C_8+)	[vol. % (db)] [g/Nm^3 (db)]	1 45	
H_2O	[vol. % (wb)]	25	2
O_2	[vol. % (db)]		4

The gasification occurs in a steam atmosphere within a riser, while the combustion that provides the necessary heat occurs in a bubbling fluidized bed to which residual char is transferred. The gasification temperature is around 800 °C, while the combustor is at about 870 °C. The composition of the resulting product gas and the flue gas is shown in table 4. The small amount of N_2 in the product gas is mostly the result of a small purge of the feeding system. The MILENA gasification system has been initially demonstrated on a small scale (25 kWth) [35] in a laboratory and based on these experiences, a pilot scale plant has been designed and completed in 2008 [36, 37].

3. Systems Based on Heat Exchangers

This category of gasifiers comprises of systems that use heat exchangers to transfer heat from external source (e.g., combustor) to the gasification zone. Examples of this type of allothermal gasifiers has been so far less numerous and only two systems will be presented here.

3.1. Biomass Heat Pipe Reformer (BioHPR)

The concept of the BioHPR reactor has been under development since 1999 at the Technical University of Munich [38]. It relies on sodium-based high temperature heat pipes, to transfer heat from the combustion zone to the gasification zone. The sodium heat pipes have a useful range of heat transfer applicability from approx. 600 to 1200 °C [39], and are therefore well suited for application in allothermal biomass gasifier. The principle of the BioHPR reactor is schematically shown in Figure 6 together with the principle of a high temperature heat pipe.

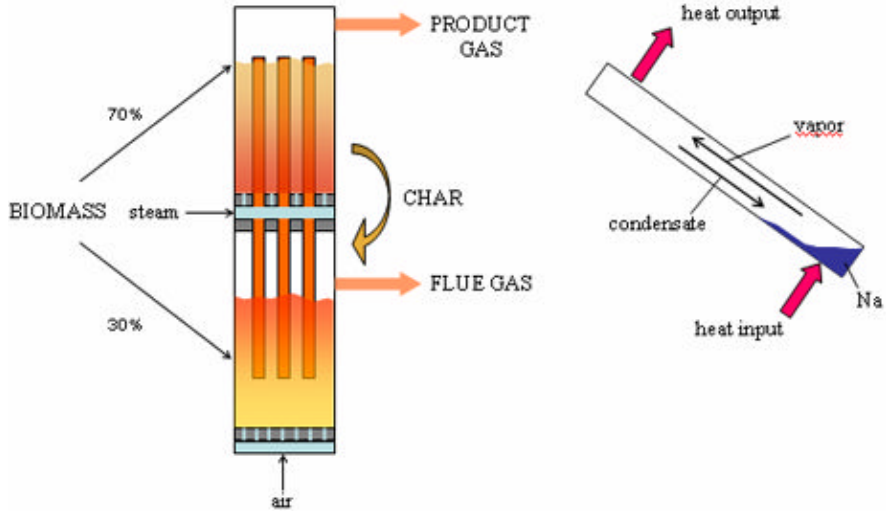

Figure 6. Schematics of the BioHPR reactor and a sodium heat pipe.

The biomass feedstock is split into two streams. Approximately 70 % of the biomass is fed into the gasification zone, where it is converted in a bubbling fluidized bed of sand, suspended by steam, into gaseous and solid products. The product gas is led away for further processing, while the solid products (i.e., char, coke) are separated and transferred to the combustion zone. The combustion zone is a bubbling fluidized bed of sand, fluidized by air. In the combustion zone, the char and the remaining 30 % of biomass feedstock is combusted in air, releasing heat. This heat is then transferred by heat pipes to the gasification zone, driving the endothermic reactions therein. The heat transfer occurs by the means of evaporation and condensation of the working fluid within the heat pipe (e.g., sodium). The sodium evaporates at the end of the heat pipe, immersed in the fluidized bed combustor. The vapor rises to the other end of the heat pipe, which is immersed in the fluidized bed gasifier. There the sodium vapor condenses, thus transferring the heat needed for the gasification. The condensed sodium then flows back to the bottom of the heat pipe.

So far, the concept of the heat pipe reformer has been successfully demonstrated on a laboratory scale [40], generating medium heating value product gas (11 MJ/Nm^3). The system has been used for a number of theoretical and experimental studies on the use of the product gas in micro gas turbines, fuel cells, or for production of hydrogen [41-45]. The concept of using heat pipes as a means of transferring heat between combustion and gasification zone in an allothermal gasifier is an attractive one, however, pilot scale demonstration of the system is needed, before wider take-up of this technology can be achieved. One of the latest developments has been the commissioning of the first commercial plant based on the BioHPR technology, in Neufahrn (Germany), in early 2008 [46].

Table 5. product gas composition from the BioHPR reactor

H_2	CO	CO_2	N_2	CH_4	C_2H_4	unit
44	20	19	7	7	2	[vol. % (db)]

3.2. PulseEnhanced™ Steam Reforming Technology

The technology based on combination of pulse combustion and steam reforming of carbonaceous fuels has been developed by the Manufacturing and Technology Conversion International, Inc. (MTCI) [47] and has been patented as the PulseEnhanced™ steam reforming technology.

The main components of the system, schematically shown in Figure 7, are the pulse combustor with resonance tubes incorporated into a fluidized bed reformer. This combination allows for high heat transfer rates between the combustion flue gases (within the resonance tubes) and the fluidized bed reformer [48, 49].

The crucial part of this system is the pulse combustor [50 - 53]. Detailed description of pulse combustion is beyond the scope of this chapter and therefore only a simplified description will be given. In principal, pulsed combustor can be compared to a four cylinder combustion engine, however without any moving parts. The claimed benefits of pulse combustion include enhanced heat-release rates in the combustion chamber and increased heat-transfer rates in the resonance tubes, compared to conventional fire tubes. It is the high

heat transfer rate that makes the pulse combustor system suitable for use in allothermal gasification.

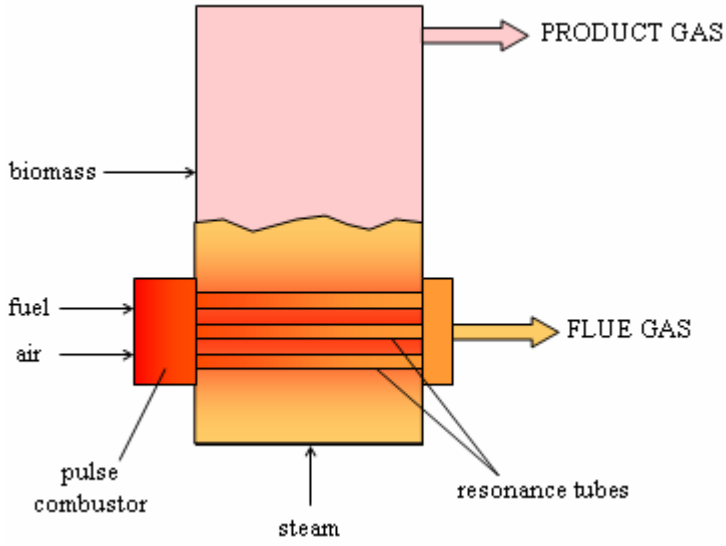

Figure 7. The schematics of an allothermal fluidized bed gasifier with pulse combustor.

This system was first demonstrated in a 12 t/day pilot-scale facility in Santa Fe Springs, using various waste and biomass feedstock [47]. Further development and testing of the technology had been done in a 50 t/day facility in Baltimore, with financial support from DOE [50]. These trials were using both subbituminous coal and biomass (e.g., wood chips and wheat straw) as feedstock. [54, 55]. Following these trials, a number of further trials in different settings were planned and conducted [56], however, detailed information on these projects are difficult to find in the public domain.

CONCLUSION

This chapter reviewed the most important developments in the field of allothermal biomass gasification in the past decade, focusing on technologies that reached the demonstration stage. From this review, it is clear that at the moment, most systems rely on the use of solid heat carriers as the means of transferring heat into the gasification zone. Systems using heat exchangers are less numerous, however, promising results have been achieved. Several allothermal gasification processes have been brought to, or very close to, commercial deployment, and in a near future we should witness wider take-up of the technology.

There is a considerable amount of underpinning research, both previous and ongoing, that could not be sufficiently covered within the scope of this chapter. However, for anyone interested in details of these technologies, there is a vast amount of information available in the public domain, and the references cited in this chapter should be a good starting point.

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Chapter 8

MODELLING FIXED-BED BIOMASS GASIFIERS: A REVIEW

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ABSTRACT

Fixed-bed gasifiers are comparatively cheap to operate as they do not require the high pressures and small particle sizes required by fluidised bed gasifiers. There is a wide variety of biomass feedstocks that can be used in a fixed-bed gasifier. Wood is a common feedstock, but bark and other agricultural residues have also been used.

In fixed-bed gasifiers the different reaction stages (pyrolysis, combustion and reduction) occur within specific regions of the gasifier. This means that the different regions of the gasifier (e.g. the gas-char reduction zone) can be modelled separately.

Numerous models have been developed to simulate the processes occurring within fixed-bed gasifiers. The assumptions made and the processes simulated vary depending upon the available input data, operating conditions of the gasifier and the purpose of the model. In this review we examine the different strategies that have been used to model fixed-bed gasifier performance.

1. INTRODUCTION

Gasification has a long history as a means to convert a solid fuel into a gaseous fuel. Coal has been widely used as a feedstock for gasification. Recently, given concerns about the environmental impacts of fossil fuel use, there has been increased interest in the use of biomass as a feedstock.

There is a wide variety of potential biomass feedstocks, gasifier designs and operating conditions for a gasification system. Process-based models are useful tools for designing and optimising the operating conditions of a biomass gasifier.

The many processes that occur during gasification are influenced by a wide range of factors such as the feedstock type, particle size, gasifier type and operating conditions. No model comprehensively covers all processes for all gasifier types under all operating conditions. Instead, models tend to focus on the processes considered most important for a particular gasifier type under likely operating conditions.

In this chapter we provide an overview of the various modelling approaches that have been used to model fixed-bed gasifiers, and focus specifically on recent studies that model fixed-bed gasifiers. As an advance on earlier gasification models (e.g. Gumz 1950), more recent models are able to take into account the results of the latest experimental measurements and use the increased computing power available. Models of other gasifier types (e.g. fluidised beds) may also have some components that could be applied to a fixed-bed gasifier. However, we restricted ourselves to considering only those models explicitly designed for fixed-bed gasifiers.

The most common fixed-bed gasifiers are the downdraft and updraft gasifiers (also referred to as concurrent and counter-current), as illustrated in Figures 2.1(a) and (b). These gasifier configurations are sometimes referred to as "moving beds" when there is continuous addition of fresh fuel and removal of char. Compared with fluidised bed gasifiers (in which a bed of fine particles is "fluidised" by high velocity air), updraft and downdraft gasifiers can be comparatively cheap to run as they do not require high pressure or fine feedstock particles. Feedstocks in fixed-bed gasifiers are generally >~3 mm in size but <~50 mm.

From a modelling perspective, fixed-bed gasifiers are interesting because the different reaction stages (pyrolysis, combustion and reduction) are spatially separated. This means different regions of the gasifier (corresponding to different processes) can be modelled separately.

2. GASIFIER CONFIGURATION AND OPERATION

Figures 2.1(a) and (b) illustrate typical downdraft and updraft gasifier configurations. In the downdraft gasifier (Figure 2.1(a)), the gasifying agent (typically air) is fed into the middle of the bed, which becomes the combustion zone. The heat of combustion pyrolyses the nearby fuel. The pyrolysis products are then drawn through the combustion zone where the temperature is high enough to thermally crack and oxidise any tars that have been produced. In practice, the level of tars that will be in the product gas is a function of temperature. The resulting gases are further reduced in the lower part of the gasifier bed by reactions with the char surface. Downdraft gasifiers are capable of producing an essentially tar-free gas. However, the need to ensure there is sufficient oxygen available throughout the entire cross-section of the combustion zone does constrain the physical dimensions of a downdraft gasifier.

In an updraft gasifier, oxidation of char occurs at the bottom of the gasifier. The heat from this exothermic reaction drives the other processes in the gasifier. In the region above the oxidation region the high temperature favours the reduction of the rising CO_2 and H_2O. Finally, at the top of the gasifier the heat from the rising product gas pyrolyses the incoming fuel.

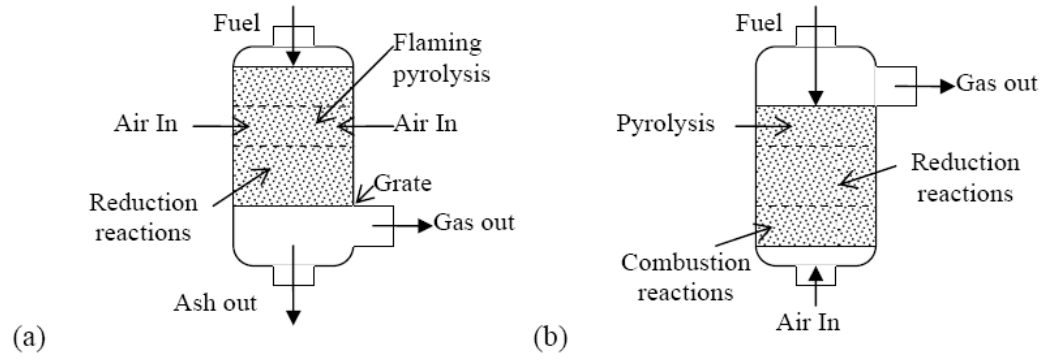

Figure 2.1. Schematic of a typical (a) downdraft and (b) updraft gasifier.

The disadvantage of this design is that the pyrolysis products are mixed with the outgoing fuel gas, and the product gas will therefore have a high tar content. Although tar has a high heating value it is liable to condense and foul downstream equipment. So, for applications other than direct burning, the product gas requires extra cleaning before it can be used.

A variation of the updraft gasifier, called the top-lit updraft gasifier, is discussed in Saravanakumar et al. (2007). In this configuration the air was blown in through the bottom of the bed but a layer of charcoal was added to the top of the bed and lit. This caused the combustion region to start at the top of the bed and travel towards the grate. As the combustion zone moved down the bed it left a layer of char above it. In this configuration therefore the pyrolysis products were still forced to travel through the hot combustion zone and a bed of char before exiting the gasifier. This meant that the top-lit updraft gasifier produced less tar than the standard updraft gasifier.

Other fixed bed variations include the staged downdraft gasifier, where the drying and pyrolysis region is physically separated from the combustion and reduction zone, and the crossdraft gasifier, where the direction of gas flow is at 90° to the direction of biomass travel.

Changes can also be made to the operating conditions of the gasifier that will change its performance. While air is a common gasifying agent, other gases such as pure oxygen, steam or carbon dioxide (CO_2) may be added, which will alter the final gas composition. The flow rate of the inlet gas can be altered. However, this does not necessarily result in a change in air-to-fuel ratio as the additional air may simply cause the fuel to be consumed faster.

Some gasifiers heat the incoming air before it enters the gasifier. Yang et al. (2006a) found that increasing the temperature of the feed gas increased the lower heating value (LHV) of the product gas, although there was a critical air temperature above which pre-heating was no longer efficient. The physical dimensions of the gasifier can also affect its operation, particularly the length of the gasifier bed, which influences the residence time of the gases in the gasifier.

Finally, the nature of the feedstock affects the gasifier performance. Both the chemical properties of the feedstock (e.g. ash, volatiles and moisture content) and the physical properties (e.g. particle size, bed porosity) can influence gasifier performance. Hanaoka et al. (2005) investigated the relationship between the gasification conversion and gas composition for air-steam gasification of woody biomass with the relative amounts of cellulose, xylan and lignin in the biomass. However, most modellers use either the ultimate (elemental) or

proximate (volatiles, char and ash) composition of biomass as model input. In general, biomass feedstocks have a higher volatile content than coals.

3. PROCESSES OCCURRING WITHIN GASIFIERS

The fuel in a gasifier is subject to the processes of drying, pyrolysis (devolatilisation), tar cracking, combustion, and char reduction. In fixed-bed gasifiers these processes, discussed in more detail below, occur in specific zones of the bed (although these zones may overlap).

3.1. Drying

Drying is the endothermic process of moisture evaporation from the feedstock. Often the feedstock will be partially dried before entering the gasifier; however, it is usually not economic to dry the feedstock completely.

Although many models do not explicitly consider drying as a separate process and subsume it into the pyrolysis process (e.g. Sharma 2008a,b), other modellers do include expressions for the rate of moisture evaporation, e.g. Di Blasi (2000, 2004) and Yang et al. (2006a,b).

3.2. Pyrolysis and Cracking

The pyrolysis process has received considerable attention as pyrolysis reactors are a potential means of producing liquid fuels from biomass. Di Blasi (2008) has reviewed the current status of pyrolysis modelling. Pyrolysis in a gasifier tends to be faster and at higher temperature than in a pyrolysis reactor. In fact, pyrolysis often occurs simultaneously with combustion in a process called "flaming pyrolysis".

Pyrolysis is the thermal decomposition of matter. For biomass gasification, pyrolysis can be represented as:

$$BIOMASS \xrightarrow{heat} CHAR + VOLATILES$$

The volatiles produced tend to be heavy organic compounds (referred to as tars) that can cause problems for downstream processes if they are not removed from the final gas stream. At high temperatures these heavy molecules can be further "cracked" into lighter molecules such as CO, CO_2, CH_4, H_2 and H_2O. This process is sometimes called "secondary pyrolysis".

Many models of fixed-bed gasifiers do not simulate the pyrolysis zone and instead assume a starting point where the biomass has already been pyrolysed to char (e.g. Liliedahl and Sjöström 1997; Giltrap et al. 2003; Ollero et al. 2003; Babu and Sheth 2006; Paviet et al. 2008) or that pyrolysis is instantaneous (e.g. Mathieu and Dubuisson 2002). Other equilibrium models do not attempt to simulate the specific reaction pathways and simply predict the end products (e.g. Zainal et al. 2001; Altafini et al. 2003; Jarungthammachote and

Dutta 2006; Melgar et al. 2007; Sharma 2008a). The reaction schemes used by models that explicitly simulate pyrolysis processes are described below.

Di Blasi (2000, 2004) modelled pyrolysis as a 2-stage process, each with its own reaction rate:

$$\text{Stage 1: } BIOMASS \rightarrow CHAR + GAS_1 + TAR \quad \text{(P1)}$$

$$\text{Stage 2: } TAR \rightarrow GAS_2 \quad \text{(P2)}$$

Both of these reactions were considered to have first order reaction rates of the form:

$$R = A\exp\left(\frac{-E_A}{\Re T}\right)\rho_r$$

where R is the reaction rate ($kg.m^{-3}.s^{-1}$), A is the pre-exponential factor (s^{-1}), E_A is the activation energy ($kJ.mol^{-1}$), $\Re$ is the universal gas constant (8.314472×10^{-3} $kJ.K^{-1}.mol^{-1}$), T is the temperature (K), and ρ_r is the density of the reactant ($kg.m^{-3}$).

Wurzenberger et al. (2002) used a similar scheme for biomass pyrolysis, except that instead of using a single reaction rate for reaction P1, a separate rate was used for the production of each product species (H_2O, CO, CO_2, H_2, CH_4, tar and char). Table 3.1 refers to these reactions as PH2O, PCO, PCO2, etc.

Table 3.1 shows the constants used by different models to describe the pyrolysis reaction rates. The constants shown are A (the pre-exponential factor) and E_A (the activation energy).

Table 3.1. Kinetic constants used in models of pyrolysis

Model	Reaction	Biomass type	A (s^{-1})	E_A ($kJ.mol^{-1}$)
Di Blasi (2000)	P1	beech	1.516×10^3	105
Di Blasi (2000)	P2	beech	4.28×10^6	107
Gerun et al. (2008)	P3	wood chips	10^7	100
Gerun et al. (2008)	P4[a]	wood chips	$3.39 \times 10^{14} \times [H_2]^{-0.5}$	350
Wurzenberger et al. (2002)	PH2O	beech	3.68×10^{13}	149.5
Wurzenberger et al. (2002)	PCO	beech	9.00×10^9	111.0
Wurzenberger et al. (2002)	PCO2	beech	5.23×10^9	105.0
Wurzenberger et al. (2002)	PH2	beech	4.73×10^4	92.5
Wurzenberger et al. (2002)	PCH4	beech	1.09×10^5	71.3
Wurzenberger et al. (2002)	PTAR	beech	2.09×10^{10}	112.7
Wurzenberger et al. (2002)	P2[b]	beech	$10^{4.98}$	93.37
Yang et al. (2006)	P1	wood pellets	ns	ns

ns = not stated.

[a]The naphthalene term was raised to the power of 1.6 in this reaction rate equation.

[b] For the rate of production of each product species, A was multiplied by the stoichiometric coefficient of that species.

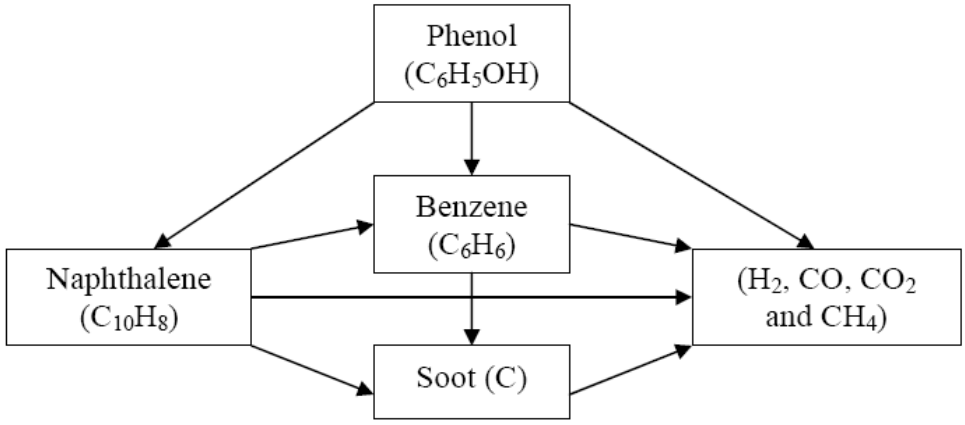

Figure 3.1. Tar mechanism from Gerun et al. (2008).

Yang et al. (2006) modelled an updraft gasifier using a pyrolysis reaction of the form of P1 above. However, instead of using reaction P2, they assumed that some of the tar was combusted by oxygen.

Gerun et al. (2008) modelled a two-stage downdraft gasifier where the pyrolysis/drying zone is physically separated from the combustion/reduction zone. It was assumed that the tar produced in the pyrolysis zone was mostly phenol. The phenol then decomposed according to the scheme in Figure 3.1. These reactions involved thermal decomposition of phenol and naphthalene, partial oxidation of compounds and reactions with steam.

The thermal tar decomposition reactions modelled by Gerun et al. were:

$$C_6H_5OH \rightarrow CO + 0.4C_{10}H_8 + 0.15C_6H_6 + 0.1CH_4 + 0.75H_2 \quad \text{(P3)}$$

$$C_{10}H_8 \rightarrow 7.38C_{(s)} + 0.275C_6H_6 + 0.97CH_4 + 0.98H_2 \quad \text{(P4)}$$

3.3. Combustion

Combustion occurs in the oxygen-rich zone of the gasifier. It is the exothermic reaction of a species with oxygen. A general formula for combustion reactions is:

$$C_xH_yO_z + (\frac{x}{2}(1+r) + \frac{y}{4} - \frac{z}{2})O_2 = x(1-r)CO + xr.CO_2 + \frac{y}{2}H_2O$$

where r varies from 0 to 1 depending on the amount of O_2 in the system relative to the fuel. The fuel to air ratio in the gasifier relative to the ratio required to completely convert the fuel to CO_2 is sometimes called the equivalence ratio. In a gasifier (as opposed to a combustor) the aim is to restrict the O_2 supply so that complete combustion of the biomass does not occur.

Two types of combustion reactions can occur in a gasifier: combustion of gases released by pyrolysis (homogeneous combustion) and combustion of the solid char (heterogeneous

combustion). Homogeneous combustion reaction rates will generally be faster than heterogeneous combustion as there is better mixing of reactants in the gas phase.

Table 3.2 shows the combustion reactions considered in a number of gasifier models. It should be noted that the pre-exponential factor has units that depend on the degree of the reaction equation with respect to reactant concentrations and the units in which the concentrations are expressed. In Table 3.2 we quote the reaction rates as given in a number of models; however, there does seem to have been some confusion between different authors. For example, both Di Blasi (2004) and Gerun et al. (2008) quote Di Blasi (2000) as the source of the reaction rate constants for the combustion of H_2. However, the pre-exponential factors used vary by a factor of 10^3 (presumably due to confusion between mol and kmol).

3.4. Char reduction

Char reduction reactions occur when hot gases react with the char surface. CO_2 and H_2O can be reduced to CO and H_2 respectively via the reactions:

$$C + CO_2 \rightarrow 2CO$$
$$C + H_2O \rightarrow CO + H_2$$

The products of these reactions are combustible when mixed with O_2, and contribute towards the heating value of the product gas. They can also combust within the gasifier if they enter a region with sufficient oxygen at high enough temperature (more likely in updraft rather than downdraft configurations). Combustion of CO and H_2 is considered in some of the model reaction schemes shown in Section 3.3.

The char reduction reactions are endothermic, absorbing energy released during combustion, and tend to stabilise the temperature. Other reactions can also occur in the char reduction zone such as CH_4 formation ($C + 2H_2 \rightarrow CH_4$) and various homogeneous gas phase reactions. Models vary in which reactions they consider important. Table 3.3 lists the reduction zone reactions considered in a number of models and the form of the controlling reaction rate expressions.

Graboski (1981) described five reaction steps that occur during char gasification:

- diffusion of reactants across the “stagnant film” surrounding the char particle to the external char surface,
- diffusion of gas down the pore towards the centre of the particle,
- adsorption, surface reaction, and desorption on the pore wall,
- diffusion of products out of the pore,
- diffusion of products across the stagnant film to the gaseous reaction environment.

The overall reaction rate is limited by different processes at different temperatures. According to Graboski (1981), surface kinetics are the rate limiting factor for temperature < 870°C; between 870 and 1315°C pore diffusion is limiting; while for temperatures > 1315°C the limiting factor is mass transfer.

Table 3.2. Combustion reactions and rate equations used in gasification models

Model	Reaction	Rate
Di Blasi (2000)	$(tar)CH_{1.522}O_{0.0228} + 0.867O_2 \rightarrow CO + 0.76$	$R = A\exp\left(\frac{-80}{\Re T_g}\right) T_g [Tar]^{0.5} [O_2]$ A = 9.2 x 10^6 ($m^3.mol^{-1}$)$^{0.5}$ $s^{-1}K^{-1}$
Di Blasi (2000)	$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$	$R = A\exp\left(\frac{-80}{\Re T_g}\right) T_g [CH_4]^{0.5} [O_2]$ A = 9.2 x 10^6 ($m^3.mol^{-1}$)$^{0.5}$ $s^{-1}K^{-1}$
Di Blasi (2000)	$2CO + O_2 \rightarrow 2CO_2$	$R = A\exp\left(\frac{-166}{\Re T_g}\right) [CO][O_2]^{0.25} [H_2O]$ $A = 10^{17.6} (m^3.mol^{-1})^{0.75} s^{-1}.K^{-1}$
Di Blasi (2000)	$2H_2 + O_2 \rightarrow 2H_2O$	$R = A\exp\left(\frac{-42}{\Re T_g}\right) [H_2][O_2]$ $A = 10^{11}$ $m^3 s^{-1}.mol^{-1}$
Di Blasi (2000, 2004)	$(char)CH_\alpha O_\beta + \gamma O_2 \rightarrow$ $(2 - 2\gamma - \beta + \alpha/2)CO + (2\gamma + \beta - \alpha/2 - 1)$	$R = \nu_p \frac{[O_2]}{(1/k_m) + 1/(5.67 \times 10^9 \exp\left(\frac{-160}{\Re T_s}\right))}$ units: $kmol.m^{-3}.s^{-1}$ ν_p = particle density number (m^{-1}) k_m = mass transfer coefficient ($m.s^{-1}$)

Model	Reaction	Rate
Di Blasi (2004)	$(tar)CH_{1.522}O_{0.0228} + 0.867O_2 \rightarrow CO + 0.761H_2O$	$R = 9.2\times10^{6}\exp\left(\frac{-9650}{T_g}\right)T_g[Tar][O_2]$ units: kmol.m^{-3}.s^{-1}
Di Blasi (2004)	$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$	$R = 9.2\times10^{6}\exp\left(\frac{-9650}{T_g}\right)T_g[CH_4][O_2]$ units: kmol.m^{-3}.s^{-1}
Di Blasi (2004)	$2CO + O_2 \rightarrow 2CO_2$	$R = 1.3\times10^{11}\exp\left(\frac{-15105}{T_g}\right)[CO][O_2][H_2O]^{0.5}$ units: kmol.m^{-3}.s^{-1}
Di Blasi (2004)	$2H_2 + O_2 \rightarrow 2H_2O$	$R = 10^{11}\exp\left(\frac{-10000}{T_g}\right)[H_2][O_2]$ units: kmol.m^{-3}.s^{-1}
Gerun et al. (2008)	$CO + 0.5O_2 \rightarrow CO_2$	$R = 1.3\times10^{11}\exp\left(\frac{-125.6}{\Re T}\right)\rho_{CO}\rho_{O_2}^{0.5}\rho_{H_2O}^{05}$ units: kmol.m^{-3}.s^{-1}
Gerun et al. (2008)	$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$	$R = 4.4\times10^{11}\exp\left(\frac{-125.52}{\Re T}\right)\rho_{CH_4}^{0.5}\rho_{O_2}^{1.25}$ units: kmol.m^{-3}.s^{-1}
Gerun et al. (2008)	$C_6H_5OH + 4O_2 \rightarrow 6CO + 3H_2O$	$R = 9.2\times10^{6}\exp\left(\frac{-80}{\Re T}\right)T\rho_{C_6H_5OH}^{0.5}\rho_{O_2}$ units: kmol.m^{-3}.s^{-1}

Table 3.2. (Continued)

Model	Reaction	Rate
Gerun et al. (2008)	$C_6H_6 + 4.5O_2 \rightarrow 6CO + 3H$	$R = 2.4\times10^{11}\exp\left(\frac{-125.52}{\Re T}\right)\rho_{C_6H_6}^{-0.1}\rho_{O_2}^{1.85}$ units: kmol.m^{-3}.s^{-1}
Gerun et al. (2008)	$C_{10}H_8 + 7O_2 \rightarrow 10CO + 4H$	$R = 9.2\times10^{6}\exp\left(\frac{-80}{\Re T}\right)T\rho_{C_{10}H_8}^{0.5}\rho_{O_2}$ units: kmol.m^{-3}.s^{-1}
Gerun et al. (2008)	$H_2 + 0.5O_2 \rightarrow H_2O$	$R = 10^{14}\exp\left(\frac{-42}{\Re T}\right)[H_2][O_2]$ units: kmol.m^{-3}.s^{-1}
Kayal et al. (1994)	$C+O_2 \rightarrow CO_2$	Gasification of bundled jute sticks. Considered to be diffusion limited and steady-state. Rate equation for gaseous reactant x into solid char: $-\frac{dN_x}{dt} = n2\pi\Delta ZD_x\left(\frac{a_x(f)}{\ln(r(f)/r(v))}\right)$ N_x = number of kmols, n = number of jute sticks in bundle, Z = height (m), D = diffusivity (m^2.s^{-1}), *a(f)* = bulk concentration of gas (kmol.m^{-3}), *r(f)* outer radius of each stick, *r(v)* radius up to char surface in core
Wurzenburger et al. (2002)	$2\frac{\eta+1}{\eta+2}C + O_2 \rightarrow \frac{2\eta}{\eta+2}CO$	$R = 1.5\times10^{6}\exp\left(\frac{-13078}{T_s}\right)\rho_{O_2}(1-X_C)^{1.2}$ units: s^{-1} X_C = the fraction of char that has been converted
Wurzenburger et al. (2002)	$2CO + O_2 \rightarrow 2CO_2$	$R = 3.98\times10^{14}\exp\left(\frac{-20119}{T_g}\right)[CO][O_2]^{0.25}[H_2O]^{0.5}$ units: mol.m^{-3}.s^{-1}

Model	Reaction	Rate
Wurzenburger et al. (2002)	$2H_2 + O_2 \rightarrow 2H_2O$	$R = 2.19\times10^{12}\exp\left(\frac{-13127}{T_g}\right)[H_2][O_2]$ units: mol.m^{-3}.s^{-1}
Yang et al. (2006a)	$C_mH_n + (m/2 + n/4)O_2 \rightarrow$	$R = 59.8T_gP^{0.3}\exp\left(\frac{-12200}{T_g}\right)[C_mH_n]^{0.5}[O_2]$ units: kmol.m^{-3}.s^{-1} P = pressure
Yang et al. (2006a)	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	$R = 1.3\times10^{11}\exp\left(\frac{-62700}{T_g}\right)[CO][H_2O]^{0.5}[O_2]^{0.5}$ units: kmol.m^{-3}.s^{-1}
Yang et al. (2006a)	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$R = 3.9\times10^{17}\exp\left(\frac{-20500}{T_g}\right)[H_2]^{0.85}[O_2]^{1.42}[C_mH_n]^{-0.56}$ units: kmol.m^{-3}.s^{-1}
Yang et al. (2006a)	Mixing rate with air: all the above gas-phase reactions were limited by the rate of mixing of the gaseous fuel with air, R_{mix}	$R_{mix} = B_{mix}(1-P)^{1/3}\rho_{gas}V.\min\left(\frac{C_{fuel}}{S_{fuel}}, \frac{C_{O_2}}{S_{O_2}}\right)/(Pl_P)$ units: kg.m^{-3}.s^{-1} B_{mix} = constant, P = pressure, V = velocity, C_x = mole fraction of species x, S_x = stoichiometric coefficient of species x in reaction, l_P is characteristic length
Yang et al. (2006a)	$C_s + rO_2 \rightarrow 2(1-r)CO$ where $r = 2500\exp(-6420/T)$	$R = \frac{P_{O_2}}{1/k_r + 1/k_d}$ P_{O_2} = partial pressure of oxygen k_r, k_d = reaction rate constants due to chemical kinetics and diffusion respectively

Table 3.2. (Continued)

Model	Reaction	Rate
Yang et al. (2006b)	$C_mH_n + \frac{m}{2}O_2 \rightarrow mCO$	$R = 59.8T_g^{0.3}\exp\left(\frac{-12200}{T_g}\right)[C_mH_n]^{0.5}[O_2]$ units: kmol.m^{-3}.s^{-1}
Yang et al. (2006b)	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	$R = 1.3\times10^{11}\exp\left(\frac{-62700}{T_g}\right)[CO][H_2O]^{0.5}[O_2]^{0.5}$ units: kmol.m^{-3}.s^{-1}
Yang et al. (2006b)	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$R = 3.9\times10^{17}\exp\left(\frac{-20500}{T_g}\right)[H_2]^{0.85}[O_2]^{1.42}$ units: kmol.m^{-3}.s^{-1}
Yang et al. (2006b)	Mixing rate with air: all the above gas-phase reactions were limited by the rate of mixing of the gaseous fuel with air, R_{mix}	$R_{mix} = B_{mix}\rho_g\left(150\frac{D_g(1-\phi)^{2/3}}{d_p^2\phi} + 1.75\frac{V_g(1-\phi)^{1/3}}{d_p\phi}\right)\min\left(\frac{C_{fuel}}{S_{fuel}}, \frac{C_{O_2}}{S_{O_2}}\right)$ units: kg.m^{-3}.s^{-1} B_{mix} = constant, D_g = dispersion coefficient of species, ϕ = void fraction in bed, d_p = particle diameter (m), V_g = y-velocity (m/s), C_x = mole fraction of species x, S_x = stoichiometric coefficient of species x in reaction, l_P is characteristic length
Yang et al. (2006b)	$C + \alpha O_2 \rightarrow 2(1-\alpha)CO$	$R = \frac{A_p[O_2]}{(1/A_r\exp(-E_r/\Re T_s)) + (1/k_d)}$ units: kmol.m^{-3}.s^{-1} A_p, A_r = pre-exponential factors, k_d = char burning rate constant as a result of diffusion

Note: [X] denotes the molar concentration of species X (in mol.m^{-3} or kmol.m^{-3}), ρ_x is the density of species X in kg.m^{-3}. $\Re$ is the universal gas constant (= 8.314472x10^{-3} kJ.K^{-1}.mol^{-1}). T_s is the temperature of the solid phase, T_g is the temperature of the gas phase (both in K).

Table 3.3. Char reduction reactions and rates equations used in models[1]

Model	Reaction	Rate
Di Blasi (2000)	$CO + H_2O \leftrightarrow CO_2 + H_2$	$R = A\varepsilon \exp\left(\frac{-12.6}{\Re T_g}\right)\left([CO][H_2O] - \frac{[CO_2][H_2]}{0.0265\exp(65.8/\Re T_g)}\right)$ units: kmol.m^{-3}.s^{-1} A = 2.78 m^3.mol^{-1}.s^{-1} ε = porosity
Di Blasi (2000)	$CH_\alpha O_\beta + CO_2 \rightarrow 2CO + \beta H_2O + \left(\frac{\alpha}{2} - \beta\right)H_2$	$R = \nu_p\left(\frac{[CO_2]}{(1/k_m) + 1/(A\exp(-218/\Re T_s))}\right)$ units: kmol.m^{-3}.s^{-1} A = 7.92 x 10^4 m^3.mol^{-1}.s^{-1} ν_p = particle density number (m^{-1}), k_m = mass transfer coefficient (m.s^{-1})
Di Blasi (2000)	$CH_\alpha O_\beta + \left(2 - \frac{\alpha}{2} + \beta\right)H_2 \rightarrow CH_4 + \beta H_2O$	$R = \nu_p\left(\frac{[H_2]}{(1/k_m) + 1/(A\exp(-218/\Re T_s))}\right)$ units: kmol.m^{-3}.s^{-1} A = 7.92 m^3.mol^{-1}.s^{-1} ν_p = particle density number (m^{-1}), k_m = mass transfer coefficient (m.s^{-1})
Di Blasi (2000)	$CH_\alpha O_\beta + (1-\beta)H_2O \rightarrow CO + (1 - \beta + \frac{\alpha}{2})H_2$	$R = \nu_p\left(\frac{[H_2O]}{(1/k_m) + 1/(A\exp(-218/\Re T_s))}\right)$ units: kmol.m^{-3}.s^{-1} A = 7.92 x 10^4 m^3.mol^{-1}.s^{-1} ν_p = particle density number (m^{-1}), k_m = mass transfer coefficient (m.s^{-1})

[1] Non-combustion, homogeneous gas phase reactions have also been included.

Table 3.3. (Continued)

Model	Reaction	Rate
Di Blasi (2004)	$CO + H_2O \leftrightarrow CO_2 + H_2$	$R = A\varepsilon \exp\left(\frac{-1513}{T_g}\right)\left([CO][H_2O] - \frac{[CO_2][H_2]}{0.0265\exp(3966/T_g)}\right)$ units: kmol.m^{-3}.s^{-1} A = 2.78 m^3.mol^{-1}.s^{-1} ε = porosity
Di Blasi (2004)	$CH_\alpha O_\beta + CO_2 \rightarrow 2CO + \beta H_2O + \left(\frac{\alpha}{2} - \beta\right)H_2$	$R = \frac{6(1-\varepsilon)}{d_p}\left(\frac{[CO_2]}{(1/k_m) + 1/(10^7 \exp(-26095/T_s))}\right)$ units: kmol.m^{-3}.s^{-1} ε = porosity, d_p = particle diameter (m), k_m = mass transfer coefficient (m.s^{-1})
Di Blasi (2004)	$CH_\alpha O_\beta + \left(2 - \frac{\alpha}{2} + \beta\right)H_2 \rightarrow CH_4 + \beta H_2O$	$R = \frac{6(1-\varepsilon)}{d_p}\left(\frac{[H_2]}{(1/k_m) + 1/(10^4 \exp(-26095/T_s))}\right)$ units: kmol.m^{-3}.s^{-1} ε = porosity, d_p = particle diameter (m), k_m = mass transfer coefficient (m.s^{-1})
Di Blasi (2004)	$CH_\alpha O_\beta + (1-\beta)H_2O \rightarrow CO + (1 - \beta + \frac{\alpha}{2})H_2$	$R = \frac{6(1-\varepsilon)}{d_p}\left(\frac{[H_2O]}{(1/k_m) + 1/(10^7 \exp(-26095/T_s))}\right)$ units: kmol.m^{-3}.s^{-1} ε = porosity, d_p = particle diameter (m), k_m = mass transfer coefficient (m.s^{-1})
Gerun et al. (2008)	$CO + H_2O \leftrightarrow CO_2 + H_2$	$R = 1389 \exp\left(\frac{-12.56}{\Re T}\right)\rho_{CO}\rho_{H_2O}$ units: kmol.m^{-3}.s^{-1}
Gerun et al. (2008)	$CH_4 + H_2O \rightarrow CO + 3H_2$	$R = 1.65 \times 10^{11} \exp\left(\frac{-329}{\Re T}\right)\rho_{CH_4}^{1.7}\rho_{H_2O}^{-0.8}$ units: kmol.m^{-3}.s^{-1}

Model	Reaction	Rate
Gerun et al. (2008)	$C_6H_5OH + 3H_2O \rightarrow 2CO + CO_2 + 2.95CH_4 + 0.05C_s + 0.1H_2$	$R = 10^8 \exp\left(\frac{-100}{\Re T}\right)\rho_{C_6H_5OH}$ units: kmol.m^{-3}.s^{-1}
Gerun et al. (2008)	$C_6H_6 + 2H_2O \rightarrow 1.5C_s + 2.5CH_4 + 2CO$	$R = 3.39\times10^{16} \exp\left(\frac{-443}{\Re T}\right)\rho_{H_2}^{-0.4}\rho_{C_6H_6}^{1.3}\rho_{H_2O}^{0.2}$ units: kmol.m^{-3}.s^{-1}
Giltrap et al. (2003), Babu and Sheth (2006), Sharma (2008b)	$C + CO_2 \leftrightarrow 2CO$	$R = 36.16C_{RF} \exp\left(\frac{-77.39}{\Re T}\right)\left(P_{CO_2} - \frac{P_{CO}^2}{K}\right)$ units: mol.m^{-3}.s^{-1} P_x = partial pressure of species X (Pa), K = equilibrium constant, C_{RF} = char reactivity factor (constant in Giltrap et al. (2003), varied in others)
Giltrap et al. (2003), Babu and Sheth (2006), Sharma (2008b)	$C + H_2O \leftrightarrow CO + H_2$	$R = 1.517\times10^4 C_{RF} \exp\left(\frac{-121.62}{\Re T}\right)\left(P_{H_2O} - \frac{P_{CO}P_{H_2}}{K}\right)$ units: mol.m^{-3}.s^{-1} P_x = partial pressure of species X (Pa), K = equilibrium constant, C_{RF} = char reactivity factor (constant in Giltrap et al. (2003), varied in others)
Giltrap et al. (2003), Babu and Sheth (2006), Sharma (2008b)	$C + 2H_2 \leftrightarrow CH_4$	$R = 4.189\times10^{-3} C_{RF} \exp\left(\frac{-19.21}{\Re T}\right)\left(P_{H_2}^2 - \frac{P_{CH_4}}{K}\right)$ units: mol.m^{-3}.s^{-1} P_x = partial pressure of species X (Pa), K = equilibrium constant, C_{RF} = char reactivity factor (constant in Giltrap et al. (2003), varied in others)
Giltrap et al. (2003), Babu and Sheth (2006), Sharma (2008b)	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	$R = 7.301\times10^{-2} C_{RF} \exp\left(\frac{-E}{\Re T}\right)\left(P_{CH_4}P_{H_2O} - \frac{P_{CO}P_{H_2}^3}{K}\right)$ units: mol.m^{-3}.s^{-1} P_x = partial pressure of species X (Pa), K = equilibrium constant, C_{RF} = char reactivity factor (constant in Giltrap et al. (2003), varied in others)

Table 3.3. (Continued)

Model	Reaction	Rate
Kayal et al. (1994)	$C+CO_2 \rightarrow 2CO$ $C + H_2O \rightarrow CO + H_2$ $C + 2H_2 \rightarrow CH_4$ $C+ 2H_2O \rightarrow CO_2 + 2H_2$	Gasification of bundled jute sticks. Considered to be diffusion limited and steady-state. Rate equation for gaseous reactant x into solid char: $-\frac{dN_x}{dt} = n2\pi\Delta Z D_x \left(\frac{a_x(f)}{\ln(r(f)/r(v))} \right)$ N_x = number of kmols, n = number of jute sticks in bundle, Z = height (m), D = diffusivity ($m^2.s^{-1}$), *a(f)* = bulk concentration of gas ($kmol.m^{-3}$), *r(f)* outer radius of each stick, *r(v)* radius up to char surface in core
Wurzenberger et al. (2002)	$CO+H_2O \leftrightarrow CO_2 + H_2$	$R = 2.78\times10^{-3} \exp\left(\frac{-1510}{T_g}\right)\left([CO][H_2O]-\frac{[CO_2][H_2]}{K}\right)$ units: $mol.m^{-3}.s^{-1}$ K = equilibrium constant
Wurzenberger et al. (2002)	$C+CO_2 \rightarrow 2CO$	$R = 4364\exp\left(\frac{-29844}{T_s}\right)[CO]$ units: $mol.m^{-2}.s^{-1}$
Wurzenberger et al. (2002)	$C + H_2O \rightarrow CO + H_2$	$R = \frac{4.93\times10^3 \exp(-18522/T_s)P_{H_2O}}{1+11.1\exp(-3548/T_s)P_{H_2O}+1.53\times10^{-9}\exp(25161/T_s)P_{H_2}}$ units: s^{-1} P_x = the partial pressure of species X (bar)
Yang et al. (2006a)	$C_nH_{2n+2} + nH_2O \leftrightarrow nCO + (2n+1)H_2$	$R = 0.30\times10^6 T \exp\left(\frac{-125.4}{\Re T}\right)[C_nH_{2n+2}][H_2O]$ units: $mol.m^{-3}.s^{-1}$
Yang et al. (2006a)	$CO+H_2O \leftrightarrow CO_2 + H_2$	$R = \varepsilon 2.78\exp\left(\frac{-12.6}{\Re T_g}\right)\left([CO][H_2O]-\frac{[CO_2][H_2]}{0.0265\exp(65.8/\Re T_g)}\right)$ units: $mol.m^{-3}.s^{-1}$

Model	Reaction	Rate
Yang et al. (2006a)	Gas phase reactions limited by mixing rate in air	See Table 3.1

Note: [X] denotes the molar concentration of species X in kmol.m^{-3}, ρ_x is the density of species X in kg.m^{-3}.

$\mathfrak{R}$ is the universal gas constant (= 8.314×10^{-3} kJ.K^{-1}.mol^{-1}). T_s is the temperature of the solid phase, T_g is the temperature of the gas phase (both in K).

Temperatures within the reduction zone of fixed bed gasifiers are typically in the range ~750–1000°C (Senelwa 1997; Jayah et al. 2003), so both pore diffusion and chemical kinetics can be significant. Models vary in which processes they consider. Di Blasi (2000, 2004) used a combination of diffusion through the stagnant film and chemical kinetics for char oxidation and gasification, while the homogeneous gas phase reactions were described by finite rate kinetics. Yang et al. (2006a) also used a combination of pore diffusion and chemical kinetics to describe char combustion, and introduced a "mixing rate" that could act as a limit on the kinetic rate for gas-phase combustion. Kayal et al. (1994) used pore diffusion controlled reaction rates. Others (Wurzenberger et al. 2002; Giltrap et al. 2003; Babu and Sheth 2006; Sharma 2008) described the reaction rates in terms of chemical kinetics.

4. COMMON MODELLING APPROACHES

Many chemical and physical processes occur during gasification. The key to developing a useful model is to select the processes to model and the simplifying assumptions that can be made. There is little benefit from including processes that make a negligible contribution to the gasifier performance. The purpose of the model needs to be kept in mind to ensure the model is capable of predicting the relevant behaviour.

A general rule for solving systems of equations is that the number of independent equations needed is equal to the number of unknowns. Most models of gasifiers result in systems of equations that require numerical methods to solve. The following sections illustrate the physical principles frequently used to derive the model equations.

4.1. Equilibrium vs Kinetic Models

An important distinction between gasification models is whether or not they assume the gases reach chemical equilibrium. Chemical equilibrium is the point at which the Gibbs free energy is minimised. The Gibbs free energy is given by:

$$G = H - TS$$

where H is the enthalpy(kJ.mol^{-1}), T is the temperature (K) and S is the entropy (kJ.mol^{-1}K^{-1}).

For a mixture of ideal gases in chemical equilibrium, the standard Gibb's free energy change can be expressed in terms of the equilibrium constant K_{eq} as:

$$\Delta G = -\Re T \ln K_{eq}$$

where K_{eq} can be expressed for a given reaction as:

$$K_{eq} = \frac{\prod_{products} P_{i,eq}^{\nu_i}}{\prod_{reactants} P_{i,eq}^{\upsilon_i}}$$

where $P_{x,eq}$ and ν_x are the equilibrium partial pressure and stoichiometric coefficient of species *x,* respectively.

The equilibrium constant is a function of temperature. At a given temperature, the reaction will proceed in the direction that brings the actual ratio of reactants and products closer to K_{eq}. There are published tables that list K_{eq} values at different temperatures (e.g. Barin 1993).

The assumption of chemical equilibrium is reasonable when the gases have a sufficiently long residence time. Equilibrium models are also useful for determining the maximum gasifier efficiency that can be achieved under given operating conditions.

In kinetic models, the chemical reactions are considered dynamically rather than just predicting the ultimate product concentrations. Kinetic models are useful in situations where the assumption of equilibrium is not reasonable (such as updraft gasifiers where pyrolysis occurs near the top of the bed). They also have the advantage that they simulate the predominance of different reactions in different regions of the gasifier bed. As such, kinetic models are useful when designing, scaling or improving reactors.

The reaction rates depend on chemical kinetics, pore diffusion (for gas-char reactions), gas mixing (for homogeneous gas phase reactions) and mass transfer. The overall reaction rate will be limited by whichever of these processes is slowest. For gas char reactions in typical gasifier reduction zones, chemical kinetics and pore diffusion can be important.

Some models use reaction rates that are proportional to the difference between the actual product to reactant ratios and those at chemical equilibrium, others use reaction rates derived from more detailed understanding of the reaction mechanism. A few models use reaction rates that incorporate terms for both chemical reaction and diffusion. Di Blasi (2000) combines all three approaches using the difference from equilibrium concentration for the water-gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$), reaction kinetics for the gas-phase combustion, and a combination reaction-diffusion for the heterogeneous char reactions.

The rates of reactions involving char will vary, depending of the reactivity of the char. The reactivity of a char is a measure of the number (and density) of reactive carbon sites that are accessible. This varies with the type of char and also with the amount of char that has already reacted. Most biomass chars differ from coal chars in that their reactivities tend to increase with the degree of conversion. Char reactivity is discussed further in section 4.3.

For gasifiers with sufficiently long residence times and high temperatures, the results of a kinetic model should approach equilibrium. Sharma (2008b) demonstrated this by comparing an equilibrium and kinetic model of gas char reduction in a downdraft gasifier. Beyond a critical bed length the predictions of the kinetic model were close to the predictions of the equilibrium model. However, the value of the critical bed length depended upon the initial gas composition and temperature at the top of the reaction zone.

4.2. Mass and Energy Balance

Many gasification models make use of the laws of conservation of mass and energy. That is, for any volume ΔV within the gasifier the (mass, energy) accumulated in time Δt must equal the difference between the (mass, energy) entering the volume and the (mass, energy) exiting. For the mass balance, chemical reactions can result in the creation or destruction of particular species. However, the total number of atoms of each element must remain constant.

Mass Balance

Figure 4.1 shows a segment of a gasifier bed of thickness Δ*z* that is assumed to vary only in dimension (the *z*-direction). If the amount of a given chemical species *x* at time *t* is $N_x(z,t)$, then the amount at time $t+\Delta t$ can be expressed as:

$$N_x(z,t+\Delta t) = N_x(z,t) + N_{x,in} - N_{x,out} + \left(net\ amount\ \ produced\ by\ chemical\ reactions\right)$$

If the gasifier is assumed to be operating under steady state conditions then $N(z,\ t+\Delta t) = N(z,t)$ and the equation simplifies to:

$$N_{x,out} = N_{x,in} + \left(net\ amount\ \ produced\ by\ chemical\ reactions\right)$$

The net amount produced by reactions will depend on the chemical reactions selected as significant to model (for examples see Tables 3.1, 3.2 and 3.3).

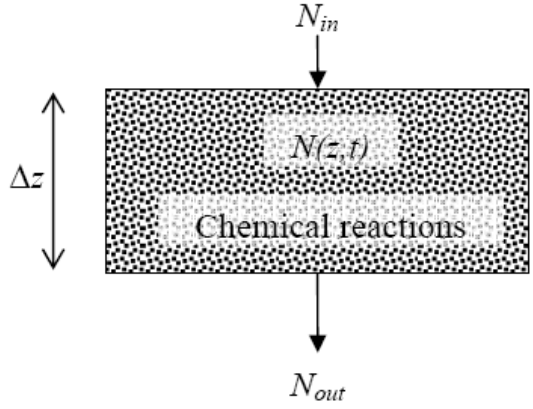

Figure 4.1. Illustration of mass balance in 1D model.

Energy Balance

The energy entering and leaving a given volume can also be balanced using a similar method to the mass balance. Figure 4.2 shows the energy flows into and out of a section of gasifier bed of thickness Δ*z*.

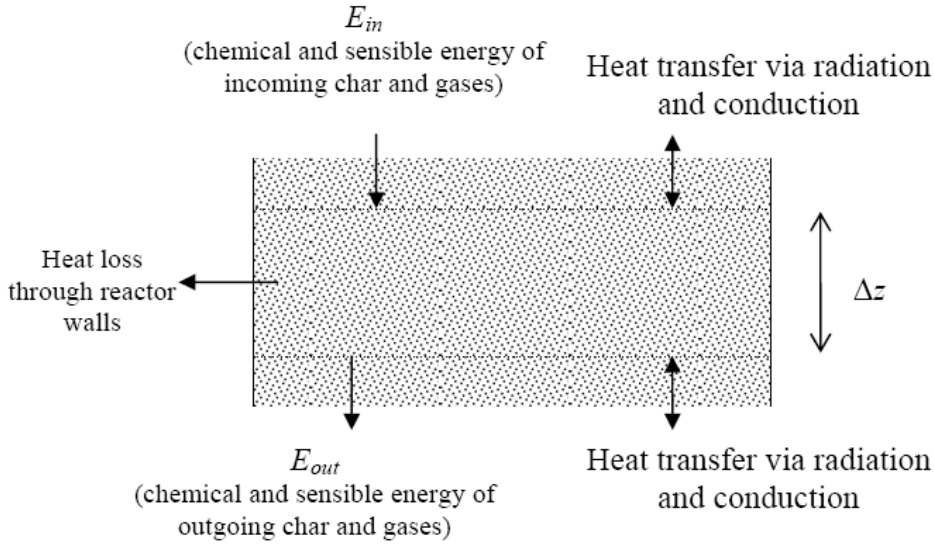

Figure 4.2. Illustration of mass balance in 1D model.

There are many potential heat transfer mechanisms. However, in practice many of the mechanisms will contribute only a small amount of heat transfer that can be neglected. For example, most gasifiers have insulated reactor walls so the heat lost through reactor walls is frequently neglected.

There are three major mechanisms for heat transfer: conduction, convection and radiation. Convection is the transfer of heat carried by matter. In fixed-bed gasifiers the flow of gases is usually forced. Matter carries heat in the form of sensible energy (the thermal energy of the hot gas or char) and chemical energy (energy embodied in creating the compound). The energy contained by N_x moles of species x at temperature T_1 is:

$$E_x = N_x \left(\int_{T_0}^{T_1} C_{P,x} dT + H^0_{f,x,T_0} \right)$$

where $C_{P,x}$ is the specific heat capacity (in $J.K^{-1}.mol^{-1}$) and H^0_{f,x,T_0} is the heat of formation of species x at a reference temperature ($J.mol^{-1}$). Frequently, the enthalpies of each substance are not accounted for explicitly. Instead, the enthaply changes (ΔH) due to the chemical reactions are used.

Conduction is the transfer of thermal energy through a material from a region of high temperature to lower temperature. The rate of heat flux (ϕ) via conduction is given by Fourier's law:

$$\phi = -k \nabla T$$

where k is the material's thermal conductivity (in $W.m^{-1}.K^{-1}$) and ∇T is the temperature gradient (in $K.m^{-1}$). Theoretically, conduction can occur in both the gas and the solid phase.

However, the thermal conductivity of char is significantly higher than the thermal conductivity of gases.

Thermal radiation is the emission of electromagnetic energy from the surface of a hot object. The energy emitted by an object is given as:

$$W = \varepsilon \sigma A T^4$$

where W is rate of energy radiation (in $J.s^{-1}$), ε is the emissivity of the material (dimensionless), σ is the Stefan-Boltzman constant ($W.m^{-2}.K^{-4}$), A is the surface area (m^2), and T is the temperature (in K).

Thermal radiation effects are often either neglected or incorporated into an "effective conductivity" of the char bed. However, Gerun et al. (2008) identified radiation as the primary means of heat transfer in the reactor core, and Sharma (2007) explicitly accounted for thermal radiation and showed that increasing particle size led to increased transfer of heat from the oxidation zone to the pyrolysis and reduction zones via radiation.

For models that consider the temperature of the gas and solid phases separately, the heat transfer between the phases also has to be considered. Wurzenberger et al. (2002) considered heat exchange between gases and particles to occur only via convection and conduction at the particle surface and ignored radiative transfers.

4.3. Char Models

Models vary in their treatment of the solid phase (char). Sometimes, unburned char is tracked (De Blasi 2000; Yang et al. 2006a; Sharma 2008a), other models assume that the char is completely consumed by the time it reaches the bottom of the gasifier (Kayal et al. 1994; Zainal et al. 2001; Melgar et al. 2007), and others neglect the char assuming that its only role is as a carbon reservoir (Giltrap et al. 2003; Babu and Sheth 2006).

Most models assume that the char particles are sufficiently small that there is no significant thermal gradient within the particle. However, for large particles the rate of pyrolysis can be limited by the rate of inward heat conduction.

The reactivity of char influences the rates of the gas-char reactions. Char reactivity, which depends on the number of active carbon sites available for reaction on the char surface, varies both with the source of the char and the degree of burnoff.

Wang and Kinoshita (1993) formulated a kinetic model for biomass gasification where the reaction rates were dependent on the fraction of char burnoff, the number of moles of actives sites per unit char surface area, char density, and its initial diameter. Giltrap et al. (2003) simplified this model by introducing a constant "char reactivity factor" (C_{RF}) that incorporated the char specific factors from the reaction rate equations in Wang and Kinoshita. The C_{RF} was found by empirical fitting to produce an exit gas temperature that corresponded to measured values. This model was further refined by Babu and Sheth (2006) who looked at using C_{RF} values that varied linearly or exponentially down the length of the bed. The varying C_{RF} factor resulted in a temperature profile down the bed that more closely matched the experimental results of Jayah et al. (2003).

The volumetric, shrinking core and the random pore models are three char models commonly used to explain changes in char reactivity as it is consumed. Fermoso et al. (2008) provided a description of these models and equations for the implied char reactivity as a function of burnoff. The volumetric model assumes that the reaction process occurs uniformly along the sample. In this case, the rate of change of the char mass fraction depends linearly on the fraction. The shrinking core (or grain) model assumes that char reactions occur on the char surface and the size of the particle slowly decreases as it is consumed (but the particle density remains constant). The random pore model assumes that char reactions occur within the pores of the particle and that as the char is consumed it becomes more porous (i.e. the particle size remains constant but the density decreases). The volumetric and shrinking core models result in the reactivity of a char decreasing with burnoff (due to reduced surface area). However, the random pore model results in a maximum char reactivity at some intermediate burnoff level as the widening pores initially increase the reactive surface area. Fermoso et al. (2008) compared the performance of these three models and found that the random pore model best predicted rates of steam gasification for four out of five different char types.[2]

In addition to the physical structure of the char particle, the presence of some minerals can act as a catalyst. For example, Senneca (2007) found the reactivity of olive husk char to be higher than pine seed shells or wood chips due to the relatively high amount of potassium oxides in the olive husk. While the microstructural properties of the chars did not explain the relative reactivities of the char, they did explain the evolution of the combustion and gasification rates with burnoff.

4.4. Summary of Recent Models

Numerous models of fixed-bed gasification have been developed. These differ in the processes considered and simplifying assumptions made. In turn, the assumptions made depend on the availability of data to parameterise and verify the model, the degree of computational complexity desired, and the ultimate purpose of the model. Table 4.1 summarises the properties of a number of these models. The chemical reaction schemes for these models can be found in Tables 3.1–3.3.

5. DISCUSSION

Given the wide range of possible variations in gasifier configuration, feedstocks, and operating conditions, it is useful to develop process-based models to predict gasifier performance with different feedstocks and operating conditions and as an aid to designing optimal gasifier configurations. As seen in section 3, numerous models have been proposed to model fixed-bed gasifiers.

[2] The fifth char type, olive stones, was not modelled well by any of the models. This was considered to be due to catalytic effects.

Table 4.1. Properties and assumptions of updraft and downdraft gasification models

Model	Gasifier type	Output predictions	Assumptions
Altafini et al. (2003)	Stratified downdraft	• Composition of output gas (without tar) • Effects of moisture content	• Chemical equilibrium • "Cycle-Tempo" model used to calculate mass, energy and chemical species balance for each reactor component • Tar formation neglected • Reaction temperature used as input • 1% heat loss from reactor
Babu and Sheth (2006)	Downdraft	• Gas composition, reaction rates and temperature profile within gasifier	• As for Giltrap et al. (2003) but with C_{RF} treated as a linearly or exponentially varying parameter
Chern et al. (1991a)	Downdraft	• Gas composition, unreacted char and exit gas temperature	• Equilibrium model • Steady state • Tars neglected • Char and wet gas exiting the system are in thermodynamic equilibrium
Chern et al. (1991b)	Downdraft	• Temperature, gas composition and char yield at exit of flaming pyrolysis zone • Influence of air/fuel mass ratio, moisture/fuel mass ratio, heat loss rate and volatility of biomass examined	• Equilibrium model of flaming pyrolysis zone • Char and gas are in thermal equilibrium when they leave the flaming pyrolysis zone • Rate of heat loss from system specified • Tar content is negligible
Di Blasi (2000)	Stratified downdraft	• Dynamic behaviour of gasifier (i.e. whether grate-stabilised or top-stabilised operation) • Profiles of gas composition, solid and gas temperature with respect to time and location • Unreacted char • Effect of varying biomass feed rate or air-to-biomass ratio	• Non-equilibrium • Non steady-state • 1-D variation in properties • Moisture evaporation diffusion limited • Shrinking core model for char • Char consists of pure carbon

Model	Gasifier type	Output predictions	Assumptions
De Blasi (2004)	Updraft	• Structure of reaction fronts and gasification behaviour as reactor throughput and air-to-fuel ratio varied • Profiles of gas composition, reaction rates, solid and gas temperature with respect to time and location • Unreacted char • Effect of varying biomass feed rate or air-to-biomass ratio	• 1-D variations in properties • Non-steady-state, non-chemical equilibrium • Included heat and mass transfer across the bed resulting from convection, diffusion and conduction • Shrinking core model for char • Solid- and gas-phase temperatures calculated separately (not in thermal equilibrium) • Solid- and gas-phase heat transfer through wall • Includes radiative heat transfer through porous bed • Tar reactions included
Gerun et al. (2008)	2-stage downdraft	• Temperature and velocity pattern within bed • Gas, tar and soot concentrations • Influence of air injection velocity	• 2-D axisymmetric model • Non-equilibrium • Fluid flow through air injectors simulated • Heat transfer by radiation dominant • Gas and char particles in thermal equilibrium • Turbulent gas flow
Giltrap et al. (2003)	Downdraft	• Gas composition, reaction rates and temperature profile within gasifier	• Steady state, non-equilibrium • 1-D variation in properties • Char reduction zone only • Initial temperature and gas composition from pyrolysis, combustion and cracking processes required as an input • Gas and solid phases assumed to be in thermal equilibrium • Used empirical “char reactivity factor” (C_{RF}) to describe char reactivity • Char assumed to be readily available throughout the bed • Unreacted char not calculated

Table 4.1 (Continued)

Model	Gasifier type	Output predictions	Assumptions
Gøbel et al. (2007)	2-stage downdraft	• Gas composition and temperature profile with respect to position and time within gasifier • The mass of char in the bed and the height of the bed • Char reactivity down through the char bed • Gas production rate • Influence of changing fuel feed rate, air flow and steam injection	• 1-D model • Non-steady state • No heat loss from system • Chemical equilibrium for gas-phase reactions • Langmuir-Hinshelwood kinetics for gasification reactions • No resistance to conduction of heat and diffusion of mass within char particles • Solid and gas phases in thermal equilibrium • Char consists of pure carbon • Char reactivity a function of burnoff (both porous particle and shrinking particle models used) • No tar in gasification zone
Jarungthammachote and Dutta (2007)	Downdraft	• Product gas composition and reaction temperature • Examined the effect of moisture content	• Equilibrium model • Tar neglected • Amount of O_2 used required as input
Jayah et al. (2003)	Downdraft	• Conversion efficiency along gasification zone • Gas temperature along gasification zone • Effect of chip size and moisture content	• Separate pyrolysis and gasification sub-models • Model details not given
Kayal et al. (1994)	Updraft	• Gas composition, reaction rates and temperature profile within gasifier • Effect of varying superficial air inlet velocity	• 1-D variation in properties • Non-equilibrium • Steady-state (i.e. there is no change over time) • Heat loss from reactor wall is insignificant • O_2 reacts completely within oxidation zone • Oxidation and reduction reactions diffusion controlled • Shrinking core model for char

Model	Gasifier type	Output predictions	Assumptions
Melgar et al. (2007)	Downdraft	• Producer gas composition • Reaction temperature	• Char is completely consumed by the bottom of the gasifier • The gas and solid phase are in thermal equilibrium • Pyrolysis gas assumed to be acetic acid that breaks down into CH_4 and CO_2 • Pyrolysis complete at 750°C • Neglect heat absorbed by pyrolysis • Neglect conductivity of non-pyrolysed jute stick • Equilibrium model • No heat losses from system • Tar content in final gas negligible
Rutherford (2006)	Updraft	• Producer gas composition	• Equilibrium system • Reaction temperature specified • Solid carbon allowed as product • Fuel moisture content considered separately
Saravanakumar et al. (2007)	Top-lit updraft	• Flaming pyrolysis time • Length of flaming pyrolysis and char gasification zones • Temperature profile • Gasification rate	• Top layer composed entirely of charcoal • Convective heat transfer from gas to wood particles • Radiative heat transfer in both the char and wood regions • Model not described in full
Sharma (2008a)	Downdraft	• Gas composition • Unconverted char • Gasification efficiency • Outlet gas temperature • Endothermic heat released in char bed • Influence of moisture content, pressure, equivalence ratio and initial temperature on gasifier performance	• Equilibrium model • Fuel bed is isotropic and solid particles are spherical with uniform diameter • Solid and gases are in thermal equilibrium • Char does not have to be completely consumed • Tars neglected • Heat losses to surroundings and heat transfers via conduction and radiation considered
Sharma (2008b)	Downdraft	• Unconverted char, gas composition, endothermic heat absorption rate, exit gas temperature • Influence of char bed length and reduction zone temperature examined	• Equilibrium and kinetic models presented and compared • Char is pure carbon • Models char reduction reactions (information on inflow reactants taken from upstream pyro-oxidation model) • Used linearly varying char reactivity factor

Table 4.1. (Continued)

Model	Gasifier type	Output predictions	Assumptions
Sharma (2008b)	Downdraft	• Unconverted char, gas composition, endothermic heat absorption rate, exit gas temperature • Influence of char bed length and reduction zone temperature examined	• Equilibrium and kinetic models presented and compared • Char is pure carbon • Models char reduction reactions (information on inflow reactants taken from upstream pyro-oxidation model) • Used linearly varying char reactivity factor
Paviet et al. (2008)	Downdraft	• Char conversion with time and position within bed • Influence of temperature and steam pressure on H_2O molar fraction within char bed	• Steam gasification of char (i.e. no pyrolysis) • 1-D reaction-diffusion model • Bed temperature is kept constant • Accounts for kinetic and diffusional effects on reaction rates • Inter particle diffusion and structural changes in char bed accounted for • Pseudo-steady state with respect to gas mass transfer • Assume bulk density of char remains constant and bed height varies with time • Stefan gas flows within the solid char bed considered • Experimental determination of Langmuir-Hinshelwood kinetic parameters with a random pore model used for heterogeneous reactions
Wang et al. (2007)	Top-lit updraft	• Rate of gas production • Variation in bed porosity	• Combined whole-system and pore-level model • Gas and solid phase at thermal equilibrium at the local scale • Composition of the exit gas not considered
Wurzenberger et al. (2002)	Cross-current moving bed	• Char radius within bed • Gas composition, tar mass and mass conversion with respect to bed position • Temperature, relative particle mass, water and tar mass fractions within particle	• Combined single-particle and packed-bed model • Gas phase described using 1-D Cartesian co-ordinates. Individual particles modelled using 1-D spherical co-ordinates • Temperature can vary within particle • Heat loss from reactor wall is insignificant • Equilibrium model used for drying • Primary pyrolysis heat neutral • During drying and pyrolysis particle size remains the same; particle size shrinks during combustion

Model	Gasifier type	Output predictions	Assumptions
Yang et al. (2006a)	Updraft	• Gas composition, reaction rates and temperature profile with respect to time and position in gasifier • Effect of temperature, O_2 concentration and flow rate of feed gas investigated	• 1D variation in properties • Unsteady state • Non-(chemical) equilibrium • Separate temperatures for gas and solid phases • Bed can be treated as a porous medium • Particle shape is spherical and averaged surface-volume diameter used • Tar and unreacted char accounted for
Yang et al. (2006b)	Top-lit moving bed updraft/ crossdraft[3]	• Gas composition, temperature, reaction rates and conversion efficiency profiles throughout bed • Conversion efficiency and throughput given air supply	• 2-D variation in properties • Tar and unreacted char accounted for • Propagation of flame front primarily by radiation • Biomass and waste considered
Zainal et al. (2001)	Downdraft	• Composition of producer gas • Effects of initial moisture content and temperature	• Equilibrium model – only final gas composition calculated. • Steady-state • Assumed no unreacted O_2 or char in final product • Gasification temperature required as input • Gas and char in thermal equilibrium • Heat loss from reactor wall is insignificant

[3] As the flame front and input air move in opposite directions, Yang et al. (2006b) actually describe the system as a counter-current moving bed. However, as this is the opposite of the convention used in this paper, we have renamed the system "top-lit updraft" for consistency.

These models vary in the degree to which simplifying assumptions are made about the different processes. There is a trade-off involved in deciding the degree of complexity of a model. A highly complex model can in theory simulate a wider range of gasifier operating conditions; however, the additional complexity requires more parameter values to be known or estimated. Simplifying assumptions can reduce the number of input parameters required by the model at the cost of embedding some assumptions about the gasifier operation into the model. Ideally, the more complex models can be used to determine which processes have a significant effect on the gasifier operation and which processes can be neglected in simpler models.

Validation of models is an important step. However, there are limitations to the experimental data available as it is difficult to monitor directly what is happening within an operating gasifier. There is generally reasonable availability of data regarding the output gas composition (although water vapour content is usually not quoted) and temperature profile within the bed, but there is an absence of data on the gas (and char) composition within the bed. Various studies have looked at particular processes that occur within a gasifier in isolation (e.g. char reactivity in air, Di Blasi et al. 1999; CO_2 gasification kinetics, Ollero et al. 2003) and these results can be useful for determining model parameters and the form of some relationships.

For most applications, the final gas composition is an important output as it allows the gas lower heating value (LHV) and other derived properties such as the cold gas efficiency to be calculated. It can also be important to know the throughput of the gasifier (gas produced per unit time) if the gas is to be used in a downstream process where the rate of energy production is important.

The producer gas composition can be calculated using either an equilibrium or a kinetic model. In an equilibrium model, it is assumed that the producer gas has reached chemical equilibrium before exiting the gasifier. This is not an unreasonable assumption for some gasifiers where the gas residence time at high temperature is long enough for equilibrium to be attained. The gases produced by updraft gasifiers tend to be far from equilibrium. Equilibrium studies are also useful for determining the theoretical maximum temperatures and gas LHVs that can be obtained for a given set of operating conditions (e.g. biomass composition, air/fuel ratio, fuel moisture content).

Kinetic models track the rates of the different chemical reactions throughout the gasifier bed. Even for gasifiers where the producer gas is expected to be near equilibrium it can be advantageous to use a kinetic model in some situations. Kinetic models allow the identification of different reaction zones within the bed. This can aid reactor design by enabling, for example, the optimum bed length to be calculated.

In addition to producer gas, gasifiers can also produce ash, unreacted char, and tars. Many models neglect these components, assuming either that they are not produced in significant quantity or that they are of little interest. However, these other products can represent suboptimal conversion of biomass to energy and may have a significant disposal cost.

For some gasifier configurations (e.g. downdraft), the tar concentration in the final product is expected to be very low and it is reasonable to neglect tar production. For updraft gasifiers, however, the product gas will contain significant amounts of tars. While tar production can boost the energy content of the outlet gas if it is burned immediately, for many applications (such as electricity generation) the tar needs to be removed to prevent it from

condensing and damaging downstream equipment. For these applications, removing the tar from the product stream represents a cost. Tar production is accounted for in a number of models, all of which use some simplifying assumptions as the total number of possible tar reactions is very high.

Unreacted char is accounted for in some models. Carbon that leaves the gasifier unreacted represents biomass energy that has not been transferred to the producer gas, and disposal of unreacted char could also represent a cost. On the other hand, unreacted char could be a potential resource: there has recently been interest in using biochar produced by pyrolysis as a soil amendment to enhance soil fertility and sequester carbon (Lehman et al. 2006).

An important application of modelling gasifiers is to enable the scaling up of lab-scale reactors to commercial scale. The process of scaling up, however, is not a simple one and care needs to be taken that the assumptions made at a smaller scale are still valid at a larger scale. For example, a common model assumption is that the gases are well mixed and there is no radial variation in the gas composition. However, for a downdraft gasifier where the air is fed into the bed by a series of tuyeres around the bed circumference it becomes increasingly difficult to ensure the air penetrates the centre of the bed as the diameter increases (this is the reason many downdraft gasifiers have a constricted "throat" where the air is fed in). Other assumptions, such as the way the solid particles move through the bed and heat losses from the reactor walls, may change with scale. It is important to ensure such issues are addressed by any model being used to upscale a reactor design.

Some issues that are not usually included in models can cause problems for gasifier operation in practice. Examples include bridging (fuel lodging in the throat of the gasifier) and ash agglomeration. These tend not to be modelled, instead relying on practical solutions (e.g. Jayah et al. (2003) gave the gasifier a shake once during each run to prevent bridging), as modelling such phenomena would require a high degree of additional complexity. It is important to be aware that models cannot account for everything and there can be reasons why a modelled gasifier configuration may not perform as well in practice.

CONCLUSION

In this chapter we have reviewed recent models of updraft and downdraft gasifiers that vary in their purpose, processes considered, and degree of complexity. Although there is no "one size fits all" model suitable for all purposes, existing models do cover a wide range of chemical and physical processes. We have also given a very "broad brush" overview of many of the important processes occurring in fixed-bed gasifiers and the strategies used to model these. New models can be constructed by modifying and/or combining existing models.

The degree of model complexity selected requires some trade-off. More complex models are able to investigate the effects of a wider range of processes but this requires knowledge of a greater number of parameters that may not always be practical to obtain. Simpler models often have more reasonable data requirements but have more assumptions embedded within them and the model may need to be reparameterised (or simply may not work) when the operating conditions change.

Care needs to be taken at all times to ensure assumptions made when constructing a model are reasonable for the physical system under consideration. Over time, the model equations will be able to be improved as more experimental data become available and the underlying processes are better understood.

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Chapter 9

UPGRADING OF A BIOMASS GENERATED GAS WITH COMMERCIAL-LIKE AND HOME-MADE CATALYSTS

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ABSTRACT

Currently, biomass gasification is considered as one of the most promising thermochemical technologies converting biomass into gaseous media for the production of power or fuels. The technical feasibility of producing fuels from biomass gasification is mainly affected by the contaminants present in the gasifier product gas (H_2S, tars, fly-ash, alkali and heavy metals, ammonia etc.), that act as poison for the catalysts used in the downstream upgrading units (Steam Reforming and Water Gas Shift). A commercial-like catalyst, containing 15.3 wt.% of Ni on $MgAl_2O_4$, and a home-made catalyst, containing 4.5 wt.% of Pt and Rh (4:1 as atomic ratio) on similar support, have been exposed to the product gas of a bench-scale downdraft gasifier having output of 10 kW_{th} and fed with wood pellets and using air like gasifying agent. Untreated and exposed catalysts were deeply characterized and the extent of deactivation was examined in the model reaction of steam reforming of methane. The exposure for 52 h to the biomass-generated gas mainly affected the metal dispersion and carbon deposition, but the catalysts still achieved very good performances. The Pt/Rh system showed a lower activity than that of the Ni catalyst, but sintering and carbon formation were less pronounced.

1. INTRODUCTION

Biomass is the most promising renewable energy source that can effectively integrate the fossil fuel demand, since it furnishes almost a 10 % of the WTPES (*World Total Primary*

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Energy Supply [1], against a poor 0.5 % provided by other renewable sources nowadays much more claimed and appreciated, but available only when the sun is shining or the wind is blowing. There are several ways to produce fuels and power from biomass. Diesel blends can be obtained from vegetable oils (soybean, rapeseed) by trans-esterification of the long chain fatty acids with methanol or higher alcohols and basic catalysts. However, a considerable amount (about a 10 wt.%) of glycerol is obtained, thus starting the so called "Glycerol Challenge", a way to use this by-product instead of disposing it.

Bio-ethanol can be currently produced by fermentation of vegetable starch (sugar cane, corn and sugar beet), and Brazil is the largest producer all over the World. Bioethanol has been recently charged with being the principal cause of the increase of cereals price. Even if everyone could agree or disagree with this accusation, it is undutiful that starchy crops have a EROEI (*Energy Return On Energy Invested*) not exceeding 1.3, a very low value compared to other fuels [2,3].

However, a new technology capable to produce ethanol from cellulose (2^{nd} generation bioethanol) is under development. The use of cellulosic crops such as switchgrass would increase the EROI up to 6 [4].

The biogas, having a methane content of 50-75 vol. %, can be produced by digestion of urban waste and animal manure. It has been evaluated that a pig of 100 kg can produce up to 20 Nm^3 of methane per year. Organic matter is thus collected into digesters connected to a net of pipes that usually feed a power station, since the conversion in transport fuels is not convenient.

On the other hand, lignocellulosic biomass (wood and dedicated energy crops) and residues (bark, husks, straw, paper mill wastes) can be converted by thermal processes (pyrolysis, gasification) to liquid fuels such as Fischer-Tropsch diesel blends or dimethyl ether (a clean-burning alternative to diesel). This is of growing interest due to the high price of the crude oil and the benefit from lowering CO_2 emissions. The productivity in terms of yield and process time is very high, since thermal conversion takes place in very short reaction times (typically seconds or minutes). Pressurized biomass gasification is a central enabling technology for the clean, sustainable use of biomass for fuel generation [5]. The gas contains about 8 % of methane and 2 % of C_2 [6] that need to be upgraded to synthesis gas (CO and H_2) via steam reforming, nowadays the most used technology for syngas production from natural gas [7]:

$$CH_4 + H_2O \leftrightarrows CO + 3H_2 \ (\Delta H^0_{298} = 206 \text{ kJ/mol})$$

However, contaminants present in the biomass generated gas (fly ash, tars, H_2S, alkali metals, ammonia) may damage downstream upgrading units and poison their catalysts. In order to approach the real plant conditions as much as possible, two reforming catalysts, a commercial-like containing Ni prepared in a batch of high amount (1000 g) and an innovative noble metal based containing Pt-Rh synthesised in a batch of lower amount (100 g), have been exposed to the output gas of a bench scale downdraft gasifier. The extent of deactivation was examined in a laboratory environment, comparing the catalytic performances in the model reaction of steam reforming of methane (SRM).

2. EXPERIMENTAL

2.1. Description of the Catalysts

The commercial-like reforming catalyst is Ni on $MgAl_2O_4$ catalyst [8], prepared according to the following procedure. Aqueous slurry made up of the Mg and Al oxides and a Bohemite binder was dried at 150°C for 24 h. The dried mixture was calcined for 2 h at 800°C and then impregnated with a $Ni(NO_3)_2$ solution, dried at 150°C, and calcined at 800°C. The sample, containing a 15.3 wt. % of Ni detected by ICP-MS, has been pelletized in particles having sizes raging from 0.4 to 0.8 mm. The home-made catalyst is a Pt/Rh on $MgAl_2O_4$ that was prepared in laboratory according to the following procedure. A slurry made up of MgO and Al_2O_3, a Bohemite binder and water was dried at 150°C for 24 h. The dried mixture was calcined for 2 h at 800°C and impregnated with a $Pt(NO_3)_2$ solution, dried at 150°C, and calcined at 800°C. The platinate catalyst was impregnated by $RhCl_3$ and heated as previously. The resulting catalyst, containing 4.5 wt. % of Pt/Rh = 4.0 as atomic ratio determined by ICP-MS, has been shaped into particles having size range of 0.4 – 0.8 mm.

2.2. Characterization

Untreated and exposed catalysts were characterized by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), CHNSO analyser, N_2 ads./desorption at -196°C, X-Ray Powder Diffraction (XRPD), Temperature Programmed Oxidation combined with Mass Spectrometry (TPO-MS), Termogravimetry (TG), and H_2 chemisorption. XRPD was carried out using a Philips PW1050/81 diffractometer equipped with a graphite monochromator in the diffracted beam and controlled by a PW1710 unit (λ = 0.15418 nm). A 2θ range from 10º to 80º was studied at a scanning speed of 140°h^{-1}. Ni and Pt crystallite sizes were calculated using the Scherrer equation (Rh was not considered, since its amount was below the detection limit), respectively on the planes *hkl*: $NiO_{(2\ 2\ 0)}$: 2θCuλ = 62.8°; $Ni^0_{(2\ 0\ 0)}$: 2θCuλ = 51.9°; $Pt^0_{(1\ 1\ 0)}$: 2θCuλ = 39.8° and assuming spherical crystallites. Elemental analysis were performed in order to detect both the amount of the metals (ICP-MS) and the amount of carbon deposition (CHNSO). TG analyses were carried out on a TGA 2050 TA Instruments, by flowing air at a heating rate of 10°Cmin^{-1} up to 900°C. The TPO analyses were carried out with an O_2/He 5/95 v/v (total flow rate 20 mlmin^{-1}) gas mixture up to 900ºC on a ThermoQuest TPDRO 1100. A Boc Edwards EXC 120 Mass Spectrometer was used to analyse the gas coming out from the TPDRO 1100. Specific BET surface area assessment was performed at – 196°C by a Micromeritics ASAP 2020 instrument. The samples were pretreated by heating up to 150ºC until a pressure of 30 µmHg was reached, then kept for 30 min at this temperature, and finally heated up to 250ºC and maintained for 30 min. H_2-chemisorption analysis was done by the same Micromeritics ASAP 2020 instrument, equipped with the Chemi Tool. The sample was streamed by hydrogen for 3 h at 350°C for the Pt/Rh containing sample and at 750°C for the Ni based sample and then by helium at the same temperature for 1 h (to remove the physiadsorbed hydrogen) before performing the assay at 35°C.

2.3. Exposure to Gasifier Output Gas

The catalysts were exposed to a gas coming directly from a bench-scale downdraft gasifier working at 900°C, by connecting a slip-stream reactor to a 10 kW_{th} downdraft gasifier fed with wood chips and using air as the gasifying agent (Figure 1). A wood chip was crushed and analysed by CHNSO, showing the following composition (wt. %): C: 46.5; H: 6.1; N: 0.23; S: 0.02; O: 46.2. The product gas composition (vol. %, dry gas) measured by IR spectroscopy was: CO: 20; CO_2: 12; O_2 <0.3 and incondensable hydrocarbons between 2 and 3. The hydrogen content determined by the calorimetric method was 10 vol. %. The gas also contained 50-55 vol. % nitrogen (from balance calculations).

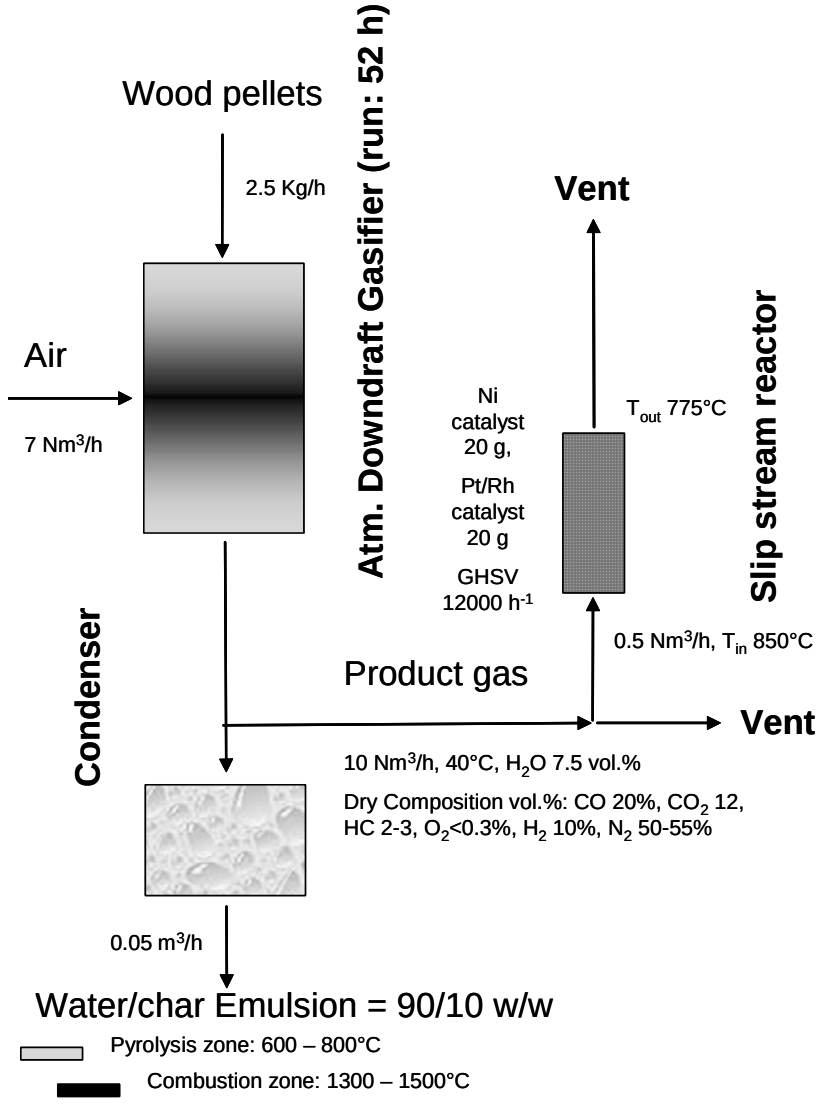

Figure 1. Sketch of the gasifier system.

2.4. Catalytic Tests

The SRM reaction was carried out in a laboratory rig using a reactor made of Incoloy 800HT in order to withstand high temperature and pressure as well as an aggressive atmosphere (Figure 2). The dimensions of the reactor tube were 50 cm in height, 30 mm in external diameter, and 9 mm in wall thickness. The reactor was inserted in an oven with two hot zones of 20 cm, capable of reaching a temperature of 1000°C. The gas flow was controlled by means of mass flow meters and deionized water was fed using an HPLC pump. The temperature was measured by means of a wired thermocouple inserted in the catalytic bed.

The test equipment was followed by two gas chromatographs for the on-line determination of the produced gas with one specific instrument dedicated to the H_2 measurement (N_2 as carrier), in order to improve accuracy. Different operational conditions were considered: pressure (P), temperature (T), steam to carbon ratio (S/C), and Gas Hourly Space Velocity (GHSV). For each run, 5 g of catalyst (5 ml of volume of the bed) have been loaded. In order to achieve a good mixing of reactants and to avoid hot spots along the reactor, SiC scales have been used to fill the tube above and below the catalytic bed. Before the runs, the fresh Ni catalyst was activated by a 100 $mlmin^{-1}$ stream of H_2/N_2 = 50:50 v/v at 700°C for 2 h, while Pt/Rh catalysts did not require any reduction step since they should be present in their metallic form after calcination at high temperature. The Ni Gas sample did not need any activation, too, since the biomass generated gas contains powerful reducers such as hydrogen and methane.

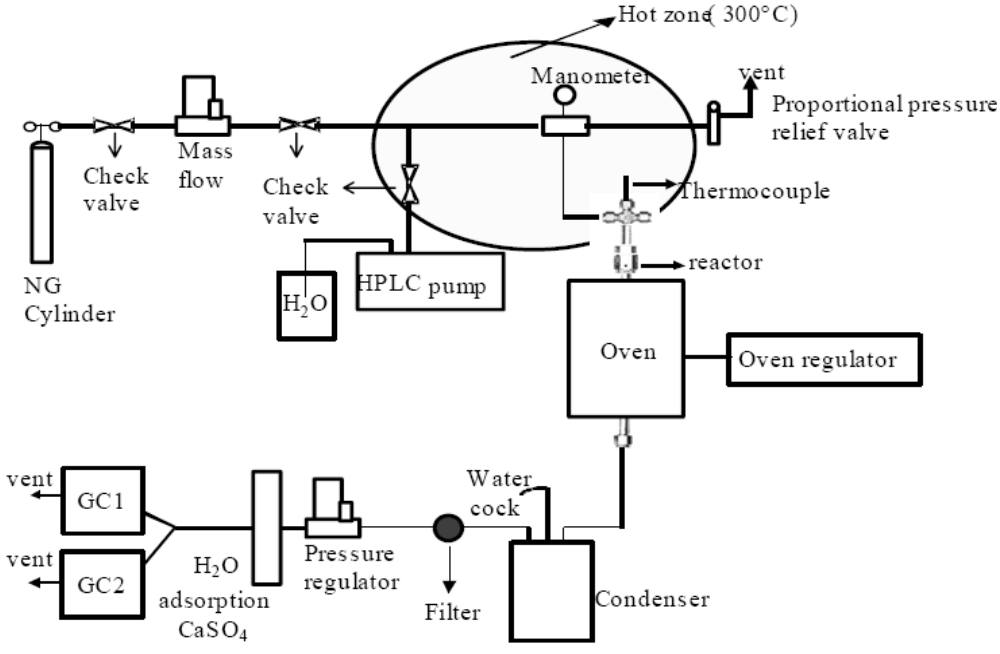

Figure 2. Scheme of the bench scale reforming plant.

3. RESULTS AND DISCUSSION

3.1. Characterization Results of the Ni Based Catalysts

The characterization results of the studied samples are shown in Table 1. The metal dispersion D, defined as the ratio of the amount of metal sites on the catalyst surface (i.e. the metal available for interaction with reactants), measured by H_2 Chemisorption, to the total amount of metal sites obtained by elemental analysis, decreased in the spent and exposed samples by sintering of the active phase, also confirmed by increased metallic crystallite size respect to the untreated sample (NiO: 17 nm). Pore clogging by the growth of sintered metallic particles was put in evidence by decreased specific BET surface area values measured by N_2 adsorption/desorption.

The metallic surface area per gram of sample, also measured by H_2 Chemisorption, is the total active metal surface area available for interaction with the adsorbate and it is related to the dispersion value. XRPD patterns of the untreated sample presented the phases of NiO, spinel $MgAl_2O_4$ and MgO. XRPD profiles of the exposed and spent samples showed the Ni phase together with $MgAl_2O_4$ and MgO, thus excluding any bulk transformation and indicating the stability of the support in the reaction conditions. CHNSO analysis showed the presence of 3.32 wt. % of carbon deposited on the Ni Gas sample, but only 0.91 wt. % remained on the Ni Gas Spent sample.

Table 1. Characterization results of the studied catalysts

	D (%)	Metallic Surface Area (m^2g^{-1})	S_{BET} (m^2g^{-1})	Metal Crystallite Size (nm)	C (wt. %)
Ni Untreated (fresh sample as prepared)	5.06	3.07	19	NiO: 17	Not detected
Ni Untreated Spent (fresh tested in the SRM reaction)	0.68	0.41	8	Ni: 34	Not detected
Ni Gas (exposed to the gasifier stream)	0.12	0.07	19	Ni: 26	3.32
Ni Gas Spent (gas exposed then tested in the SRM reaction)	0.11	0.07	13	Ni: 28	0.91
Pt/Rh Untreated (fresh sample as prepared)	3.64	0.48	16	Pt: 61	Not detected
Pt/Rh Untreated Spent (fresh tested in the SRM reaction)	0.72	0.10	16	Pt: 52	Not detected
Pt/Rh Gas (exposed to the gasifier stream)	2.94	0.39	22	Pt: 49	2.18
Pt/Rh Gas Spent (gas exposed then tested in the SRM reaction)	1.92	0.25	11	Pt: 59	Not detected

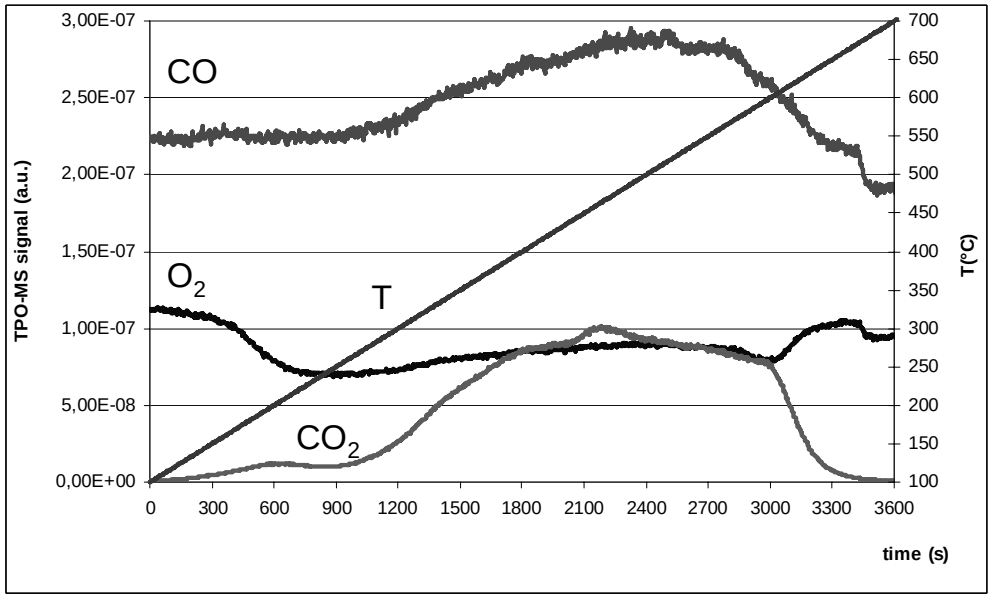

Figure 3. TPO-MS patterns of the Ni Gas sample.

In a gasifier, carbon is likely to be formed by tars condensing on the catalyst surface rather than by methane and CO dissociations [9], and feeding a clean reaction stream (pure methane and deionized water at S/C=2.5) partially removed the condensed carbon. Amorphous carbon was supposed to be deposited on the Ni Gas catalyst; otherwise XRPD pattern of the Ni Gas sample would have detected the reflections of the crystalline whiskers of graphite [10]. TGA patterns in air of the spent catalysts were not easy to clarify, since there was an increase in weight due to Ni oxidation that overlapped the weight loss due to carbon burning. In this way, the differences between the coked samples and a carbon-free reduced sample were considered, evidencing carbon amounts similar to those determined by CHNSO analysis. To investigate coke removal, TPO-MS analysis was performed (Figure 3), detecting the evolution of CO and CO_2 in the range 300-700°C, which is typical of amorphous carbon burning [11,12]. Since the end of the CO_2 plateau is considered a marker of the removal of carbon from the catalyst surface, all carbon deposits can be completely swept away feeding a diluted oxygen stream at 700°C, but eventually with the drawback of further sintering of nickel particles. The specific BET surface area of the Ni Gas sample is as high as the Ni Untreated sample. After reaction, that value decreased, in according to what happened in the Ni Untreated Spent catalyst.

3.2. Characterization Results of the Noble Metal Containing Catalysts

Metal dispersion and metallic surface area decreased in the spent and exposed samples (Table 1), like in the Ni based catalysts. However, those values are significantly higher in the Pt/Rh Gas Spent rather than in the Pt/Rh Untreated sample. XRPD patterns are similar for all the samples, showing the reflections of the phases Pt, spinel $MgAl_2O_4$ and Al_2O_3, the last added in excess during preparation in order to have all Mg segregated in the spinel phase

(differently from the commercial-like catalyst that contains a separated MgO phase, instead). No relevant changes in the textural properties of the samples occurred during exposure and reaction, thus confirming the stability of the support. The presence of carbon deposits was estimated to be 2.18 wt.% in the Pt/Rh Gas by CHNSO analysis (Table 1), matching the loss of weight of 2.0 wt.% (calculated respect to the carbon free Pt/Rh Untreated Spent sample) measured by TG analysis (Figure 4) and caused by the amounts of CO and CO_2 released by carbon burning. The TPO-MS patterns (Figure 5) clearly evidenced O_2 consumption and the emissions of CO and CO_2. In according to the open literature [13], the plateau of CO_2 at 300°C suggests that amorphous carbon was formed only. In order to have an experimental confirmation, a graphite sample was analysed in TPO-MS conditions and it started to burn at 700°C. Moreover, XRPD pattern of the Pt/Gas Gas sample did not show the reflections of the crystalline graphite.

Therefore, deposited carbon is so weak to be removed by the reaction stream (pure methane and deionized water at S/C=2.5). Indeed, the CHNSO analyser was not able to determine an appreciable amount of C in the Pt/Rh Gas Spent sample. The absence of carbon is confirmed by TG analysis, where this sample showed almost the same pattern of the carbon free spent catalyst, without evidencing any relevant weight loss. The untreated sample did not show any relevant decrease in specific surface area after reaction (Table 1). The Pt/Rh Gas presented the highest surface area value before reaction, even higher than that of the untreated sample, probably due to the deposition of amorphous carbon on the surface (rather than inside the pores), thus apparently increasing bulk surface area. During reaction, since the carbon was totally swept away, the value of the Pt/Rh Gas Spent sample halved and resulted close to that of Ni Gas Spent sample.

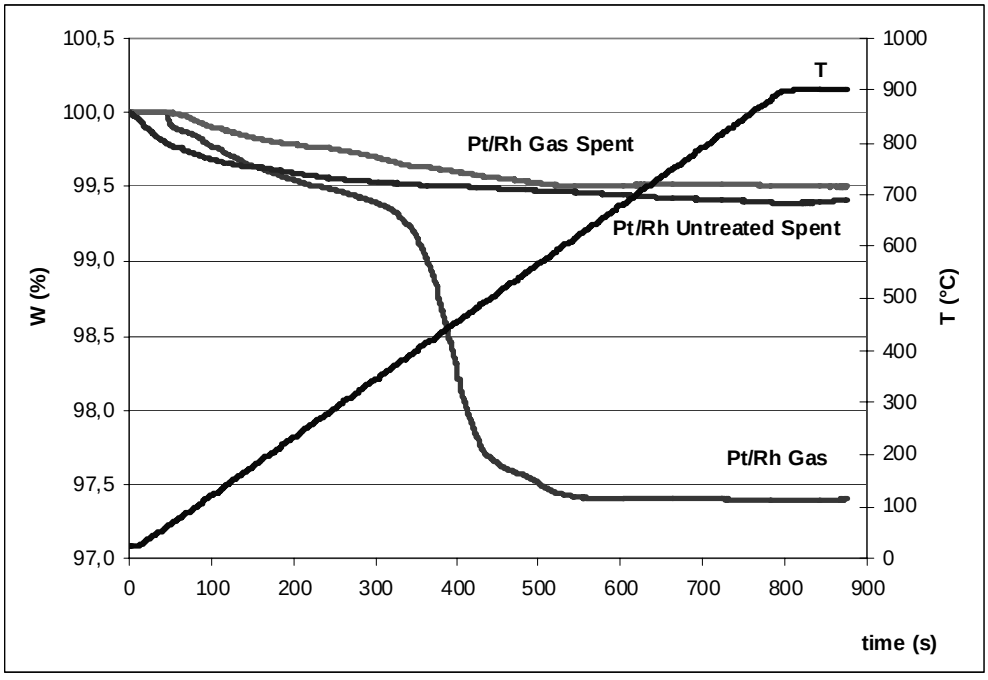

Figure 4. TG profiles of the Pt/Rh Gas sample.

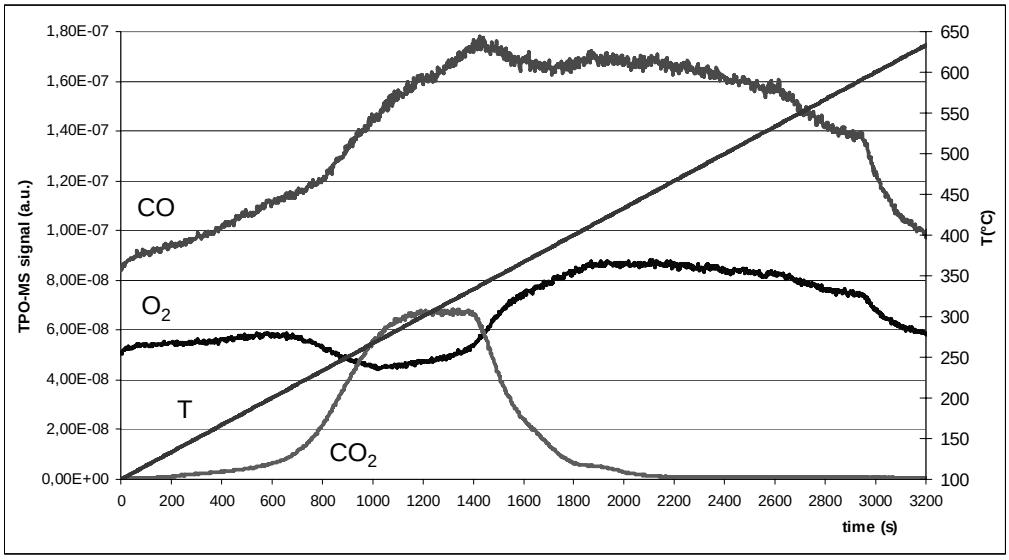

Figure 5. TPO-MS patterns of the Pt/Rh Gas sample.

3.3. Catalytic Performances

Catalytic performances of the tested materials have been evaluated in terms of methane conversion, selectivity in CO and yield in hydrogen (Figure 6), in three different operative conditions (A, B, C).

In the industrial-like condition A, where the highest conversion is achieved, all catalysts showed very good catalytic performances, except for the Pt/Rh Gas sample. In the further test B at lower conversion, carried out to better discriminate between the studied catalysts, Pt/Rh Gas sample continued to perform slightly worse than the other catalysts.

Finally, in the last test C, that catalyst seemed to recover higher performances, in according to its final value of metal dispersion (Table 1), higher than those of other spent catalysts.

The Pt/Rh Untreated catalyst performed slightly better than the Ni Untreated in the last test only, while in the previous ones no relevant differences can be detected (Figure 6).

Surprisingly, the Ni Gas sample showed the highest performances in all tested conditions, even if the amount of carbon deposits was higher (3.32 wt.%) and the sintering was more pronounced as well.

The high amount of Ni loaded on the commercial-like sample (15.3 wt.%) countervailed the higher loss of active sites, with respect to the Pt/Rh catalyst, thus justifying the highest activity.

Respect to the Ni Untreated sample, it seemed that 52 h of time-on-stream could have activated the catalyst better than the hydrogen flow in the laboratory equipment.

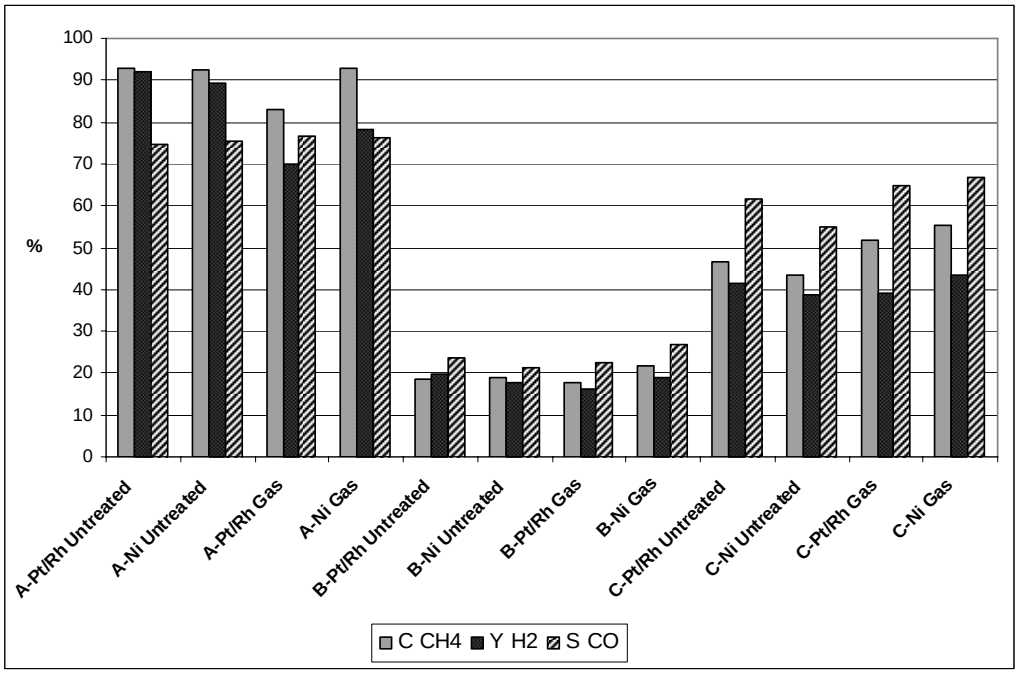

Figure 6. Comparison of the catalytic performances between the Pt/Rh and the Ni catalysts: $C_{CH4}\% = 100*(CO + CO_2)/(CO + CO_2 + CH_4)$; $Y_{H2}\% = C_{CH4}\%*H_2/(3\ CO + 4\ CO_2)$; $S_{CO}\% = 100*CO/(CO + CO_2)$; outlet compositions measured by GC. A-T_{out}=900°C; P=10 bar; V_{cat}= 5 ml; τ= 1 s; CH_4= 218 ml/min; $H_2O_{(l)}$= 0.401 ml/min; GHSV=3600 h^{-1}; S/C=2.5; B-T_{out}=600°C; P=20 bar; V_{cat}= 5 ml; τ= 0.5 s; CH_4=1517 ml/min; $H_2O_{(l)}$=1.900 ml/min; GHSV=7200 h^{-1}; S/C=1.7; C-T_{out}=700°C; P=10 bar; V_{cat}= 5 ml; τ= 0.15 s; CH_4=2269 ml/min; $H_2O_{(l)}$=2.841 ml/min; GHSV=24000 h^{-1}; S/C=1.7.

CONCLUSION

The main effect of the exposure to a biomass generated gas was a decrease in the metal dispersion. Carbon deposits were detected in the samples streamed with the biomass generated gas but they can be partially removed feeding clean methane at high S/C ratio. The commercial-like Ni catalyst showed catalytic performances slightly better than those of the Pt/Rh sample after being exposed to the biomass generated gas, due to the high Ni load that counterbalanced the phenomena of sintering and carbon formation, which were more pronounced. However, these phenomena may lead to short lifetimes, quickly deactivating the catalyst. Since stability is usually more relevant than activity in an industrial application, the noble metal system is worthy of being subdued to further and deeper investigation.

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Chapter 10

THE STUDY ON THE PERFORMANCE OF "MOBILE OXYGEN" CATALYSTS USED FOR BIOMASS GASIFICATION

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ABSTRACT

During biomass gasification process, high temperatures, high-pressure steam and sulfur containing compounds creates a severe environment for catalysts, so several attempts have been made to enhance the performance, and lots of kinds of catalysts were developed and applied. Among these catalysts, there was one kind of special catalyst with reactive oxygen species (ROS) - "mobile oxygen" in the catalysts structure. Based on the research results, these "mobile oxygen" catalysts exhibited superior resistance to carbon poisoned and/or sulfur-tolerant comparison to commercial catalyst because of these ROS. In this chapter, three kinds of the style catalysts will be illustrated respectively. Firstly, oxygen species such as dioxygen, atom adsorption oxygen and so on, relation and characteristic of these species was introduced. Then, metal "mobile oxygen" catalyst, such as Fe, Ce, Gd et al. was illustrated, the promotion by addition of these kinds of metal was introduced. Perovskite was another popular "mobile oxygen" catalyst was also mentioned. Lastly, our research on this kind of catalyst (mayenite, mayenite supported catalysts) was explained in detail.

INTRODUCTION

During biomass gasification process, complex hydrocarbons steam reforming reactions are included, which involves a risk of carbon deposition, then may reduce the performance of the catalyst in several ways, and it may eventually have to be replaced. So carbon formation is

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regarded as one main problem for deactivation of catalysts in biomass gasification process. Sulfur poisoning is another one. Product gas formed from biomass gasification process contains the major components CO, H_2, CO_2, CH_4 and H_2O, in addition to organic (tars) and inorganic (H_2S, HCl, NH_3, alkali metals) impurities and particulates. Even after a thorough desulfurizatin of the process, sulfur-containing compounds may reach the nickel catalyst at a ppb level, which is also a strong poison concentration for nickel catalysts and blocks metal active sites especially Ni-based catlaysts. So the combination of high temperatures, the presence of hydrocarbons, high-pressure steam and sulfur containing compounds creates a severe environment for catalysts, i.e. four challenges: activity, sulfur poisoning, carbon formation and sintering [1].

Several attempts have been made to enhance the sulfur tolerance and decrease in carbon formation by modifying the preparation methods [2,3] or adding accessory ingredient such as Ru [4,5], WO_3 [6,7], Pt [8,9], Rh [10,11]. However, Ru, Rh, Pt are prohibitively expensive, which results in no practical application as industrial catalysts [12]. But among these catalysts, there was one kind of special catalyst with "free oxygen" in the catalysts structure. Based on the research results, the "mobile oxygen" catalysts exhibit superior resistance to carbon poisoned and sulfur-tolerant comparison to commercial catalyst. The reasonable reason to account for such unexpected observation lies in the "mobile oxygen" in the catalysts. In this chapter, three kinds of the style catalysts will be illustrated respectively. First kind is metal "mobile oxygen" catalyst, such as Ce, Gd, Fe et al., the addition of these kinds of metal will promote activity; Second kind is mineral resources such as calcite, perovskite. Lastly, our recent research on this kind of catalyst will be introduced.

1. OXYGEN

In order to study the rules of oxidation reaction, learning the state of O in the oxide catalysts and oxygen is very important. Oxygen has two unpaired electrons in separate orbital in its outer shell. This electronic structure makes oxygen especially susceptible to radical formation.

1.1. Reactive Oxygen Species (ROS)

Oxygen adsorption on catalysts surface is very complex process, there are lot of styles, such as associative and dissociative adsorption in molecule, entering metal lattice and forming oxidation state compound. Generally, O can be divided into two groups, adsorbed oxygen and mobile oxygen (or lattice oxygen). Adsorbed oxygen is the oxygen adsorbed on the surface such as O2, CO2 and H2O, it is easy to remove them by heating or sputtering. Mobile oxygen (or lattice oxygen) is that the oxygen is bonding with cation element and forms compound. And also, by measuring the content of lattice, we can get the composition of material. In detail, main oxygen species are dioxygen (O_2), molecule adsorption oxygen (O_2^-), atom adsorption oxygen (O^-), surface lattice oxygen (O_2^-), and shown in following:

Oxygen	Superoxide anion	Peroxide	oxide anion
O_2	O_2^-	O_2^{2-}	O^-

(•) unpaired electrons

The relation of these species:

$$O_2(g) \leftrightarrow O_2(s) \leftrightarrow O_2^-(s) \leftrightarrow O_2^{2-}(s) \leftrightarrow 2O^-(s) \leftrightarrow 2O^{2-}(s)$$

Activity: $O^-(s) > O_2^{2-}(s) > O^{2-}(s)$

1.2. Characteristic of ROS

Electric conductance, work function, ESR and chemical method are usually used to characterize the oxygen species. For the dioxygen, the electric conductance will keep stable when chemical adsorption, but for ion oxygen species such as (O_2^-, O_2^{2-}, O^-, O^{2-}), the electric conductance will change obviously, then the work function will increase. So the electric conductance and work function are the main measurement to distinguish dioxygen and ion oxygen. For O^- and O_2^- can be distinguished by ESR.

In the oxygen species, beside dioxygen (O_2), for the other species, they are ions or very small molecules such as oxygen ions, free radicals, and highly reactive due to the presence of unpaired valence shell electrons.

For the application, usually atom adsorption oxygen (O^-) was applied in total oxidative reaction, surface lattice oxygen (O^{2-}) was applied in partial oxidative, and dioxygen $O_2(g)$ species usually was regarded as no reactive. "oxygen isotope" techniques can be used to distinguish these kinds species.

For example, labile O and OH species of support are usually being true active reaction intermediates in the steam reforming of hydrocarbons and oxygenates over metal oxide-supported metals. The possible contribution of oxygen vacancies or labile oxygen of support during the phenol steam reforming reaction was probed by Poly-chronopoulou [13], the steady state isotopic transient kinetic analysis (SSITKA) and the transient isotopic experiments (use of D_2O and $^{18}O_2$) experiments were done. And back-spillover of labile OH and O species from the MgO, Mg-Ce-O and Mg-Ce-Zr-O supports to the Rh and Fe metal surfaces was proven by various transient isotopic experiments.

2. "MOBILE OXYGEN" CATALYSTS

According to the stoicheometry of catalyst, most catalysts were oxygen defect compounds. So the dioxygen can be adsorbed by the surface lattice defect position and change to reactive oxygen species, then exhibit special property for redox reaction.

2.1. Metal "Mobile Oxygen" Catalysts

2.1.1. Iron Catalysts

Iron is cheap and nontoxic catalytic materials, it has several vital functions. It can serve as a carrier of oxygen, as a transport medium for electrons [14]. It shows that some catalysts by loading some amount of Fe will exhibit some high performance on the anti-carbon aspect.

Mössbauer spectroscopy is the most widely used method for the identification of iron containing materials. The technique also gives unique information on magnetic properties of compounds. The Mössbauer spectrometer (MOS) is also a unique tool for the study of the oxidation state of iron. From a Mössbauer spectrum it is possible to determine the ratio Fe^{2+}/Fe^{3+} for a given sample, within a few percent of accuracy. The precision is dependent on the number and nature of the iron containing phases present.

Mössbauer spectroscopy consists of the study of resonantly scattered (or absorbed) low energy γ-rays from ^{57}Fe in the sample under investigation. The γ-rays are produced by a radioactive source of ^{57}Co. On iron, Mössbauer spectroscopy technique demands no sample preparation. A Mössbauer backscattering spectrum gives information on the outermost layer (of a thickness of about 100 μm) of the sample under investigation. The radioactive ^{57}Co source emitting the 14.4 keV γ-rays is moved with certain selected velocity amplitudes between 4 mm s^{-1} and 12 mm s^{-1}.

I. Fe Species as the Active Site in Olivine

Olivine catalysts have been studied for steam and dry reforming of biomass and biomass tar [15-17], and olivine catalysts were used as a bed additive in fluidized bed steam gasifiers using crushed almond shells [18] and wood chips [19], in fluidized bed air gasifiers operating on a mixture of pine wood chips and olive oil residue [20], and in a secondary reactor processing the effluent from steam gasifier using beech as the biomass source [21]. In most studies, researchers found Fe species acted an important function for catalyst.

Swierczynski [16] found the formation of free Fe phases following decomposition of a Fe-bearing serpentine phase ($(Mg,Fe)_3Si_2O_5(OH)_4$) near the surface of untreated olivine catalysts, and also proved most important for facilitating higher activity compared to olivine catalysts with little or no serpentine phase initially. Thus far, Fe was assumed to be involved in the active site for the reactions. The assumption was made because previous studies on olivine catalysts demonstrated correlations between Fe and catalytic activity [17,19,20]. Additionally, the results of the present study support these claims. Catalysts with the most surface Fe and greatest reducibility were the most active. These results support metallic Fe, which is expected to be more active for C-C and C-H bond making and breaking than oxide phases, being involved as a site with high activity.

The origin of olivine catalysts and treatments prior to catalytic tests influenced the activity for $C_{10}H_8$ steam reforming was studied by Kuhn [21]. The phase in which Fe was present and its location played a strong role in understanding the differences in catalytic activity. Of the secondary phases, Fe-bearing serpentine phase enriched at the surface was judged to be the most important for achieving high catalytic activity. When it decomposed, free Fe deposited on or near the surface. Analysis of Ni-Olivine for $C_{10}H_8$ steam reforming indicated catalysts deactivation due to metallic Fe agglomeration and decreased metallic Fe dispersion.

The catalyst Ni/Olivine was examined by Mössbauer spectroscopy after toluene steam reforming at 800℃ (Figure 1) [22]. Five Fe containing components (olivine, α -Fe_2O_3, spinel phase, carbides and Ni-Fe alloys) may be characterized and their distribution is presented in Table 1. The results come from curve fitting and the values of relative percentage of iron in different phases should be considered as semi quantitative. 14% of total iron was present in the form of carbide and 8% in the form of metallic iron-together 22% of total iron that represents about 1.5 wt% Fe in the catalyst.

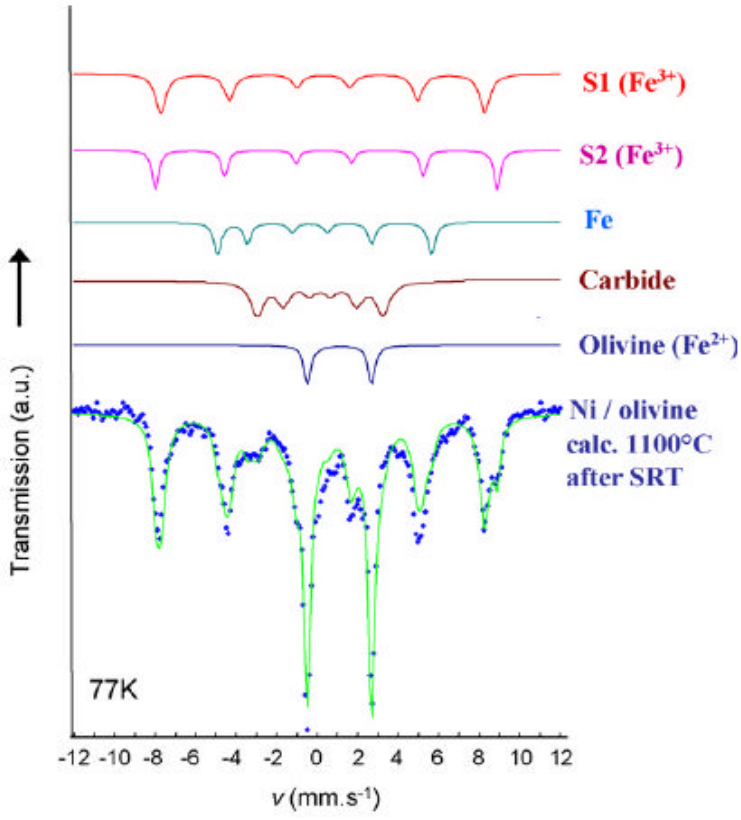

Figure 1. ^{57}Fe Mössbauer spectra at -196□(77K) of the Ni-Olivine catalyst after steam reforming of toluene (800□); the sub-spectra of the five components are indicated at top.

Table 1. Iron distribustion obtained by Mössbauer spectroscopy for Ni-Olivine after steam reforming of toluene (800℃, S/C=2.3)

Iron type	Molar percentage (%)
Fe^{2+} (olivine)	30
Fe^{3+} (α -Fe_2O_3)	11
Fe^{3+} (spinel)	37
Fe^{3+} (carbides)	14
Fe^{0} (Ni-Fe alloys)	8

II. Fe-Based Catalysts

Supported Fe catalysts of varying support chemical composition prepared by sol-gel and incipient wetness impregnation methods were studied by Polychronopoulou [23] for the steam reforming of phenol (one of the main constituents of tar produced during steam gasification of wood biomass). In this study, various supported Fe catalyst in a fixed-bed microreactor to investigate. Series catalysts was prepared and characteristic, the stability of the 5% wt Fe/50Mg/50CeO catalyst were studied during consecutive oxidation→ reaction and oxidation → reduction → reaction cycles of short duration. It is found that the most active Fe-based catalyst was 5 wt% Fe/50Mg/50CeO, a high Fe^{2+}/Fe^{3+} ratio after phenol steam reforming (Mössbauer studies) was found. Various transient experiments demonstrated that the enhanced production of H_2 occurring in the presence of supported Fe and CO_2 absorbent for short times on stream.

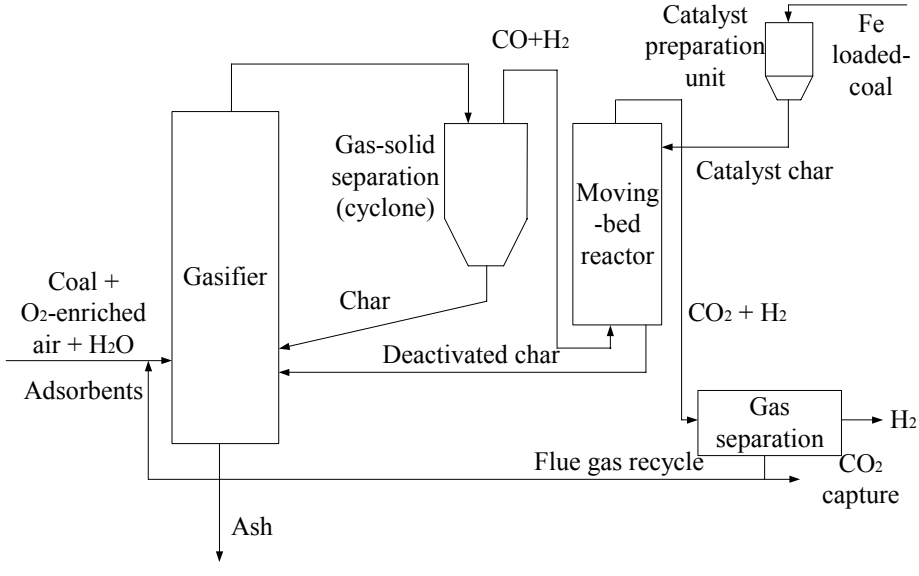

Figure 2. A schematic diagram of a conceptual process for the catalytic production of hydrogen using the char-supported nano Fe catalyst based on the gasification of brown coal.

A novel char-supported nano iron catalyst was prepared by Yu [24]. Iron is highly dispersed in the char matrix as magnetite with a particle size smaller than 50 nm. The catalyst is found experimentally to be very active for the water-gas-shift reaction at temperatures as low as 300℃. A conceptual process for the catalytic hydrogen production integrated with the gasification of brown coal (or other solid fuels such as biomass) is proposed and shown schematically in Figure 2.

In this proposed process, a moving-bed reactor, charged with char-supported nano iron catalyst, carries out various functions and could be integrated with an ordinary gasification unit without significant modifications to the gasifier facility. The proposed process does not suffer from the catalyst disposal problem as the spent catalyst is sent to the gasifier to be gasified. The production of the catalyst uses the same brown coal as that for main gasification as well as Fe-containing material such as $FeCl_3$ that is a waste from iron and steel industry. The low contents of ash-forming species in the brown coal also offer the possibility to recover Fe from the gasifer ash.

III. Fe Oxide-Based Catalysts

Calcined dolomites (CaO-MgO) from four different quarries have been tested for the upgrading of the hot raw gas from a fluidized bed gasifier of biomass with air [25]. It can found that the activity of the dolomite for tar elimination can increase by 20% on increasing its Fe_2O_3 content.

Iron-based catalysts were developed by Uddin [26] for the complete destruction of tar derived from biomass gasification by steam reforming, and also the re-generable property of iron-based catalyst was tested. Catalytic gasification of wood (Cedar) biomass was carried out using a flow-type reactor in a two step process. Temperature programmed non-catalytic steam gasification of biomass was performed in the top bed at 200-850℃, followed by the catalytic gasification of tar (and volatile matters) in the bottom bed at a constant temperature, mainly 600℃. Iron oxide (Fe_2O_3), which transformed to Fe_3O_4 during the gasification reaction, possessed catalytic activity in biomass tar gasification. The tar could be gasified by the use of iron oxide catalyst. Iron oxide catalyst also affected the composition of the gaseous products of biomass decomposition: Compared to the non-catalytic gasification, the production of H_2 and CO_2 increased, while the production of CO decreased in the presence of iron oxide catalyst which catalyzed the water gas shift reaction in addition to the decomposition of the tar fraction. And it also found the surface area of the iron oxide catalyst played an important role in the catalytic tar decomposition, the addition of γ-Al_2O_3 to ion oxide was one method for the improvement of the surface area without deactivation.

Consideration of the mechanism of biomass tar decomposition on Fe-based catalysts, Poly-chonopoulou et al. think that the absorption-enhanced are the main factor for supported Fe catalysts [23], and also the derived hydrocarbon fragments from the phenoxy adsorbed species are oxidized by labile O and/or -OH species of support via a back-spillover process [13], and by –OH groups residing on iron oxides surfaces to form H_2, CO and CO_2 and water gas shift reaction also occurs, further contributing to H_2 and CO_2 formation. Nakazawa suggested that phenol was adsorbed dissociatively on the iron oxide surface to form surface phenoxy species [27].

Uddin [26] proposed the mechanism of decomposition of biomass tar over the iron oxide catalyst, and shown in Figure 3. The surface iron (-Fe) connected to bulk iron oxide Fe_3O_4

reacts with biomass tar to produce CH_4, C_2H_4, H_2O, CO and H_2 in the first stage of the reaction over the ion oxide catalyst. Then, the produced CO is converted to CO_2 and H_2 by water gas shift reaction occurred over the iron oxide active site (surface hydroxyl group).

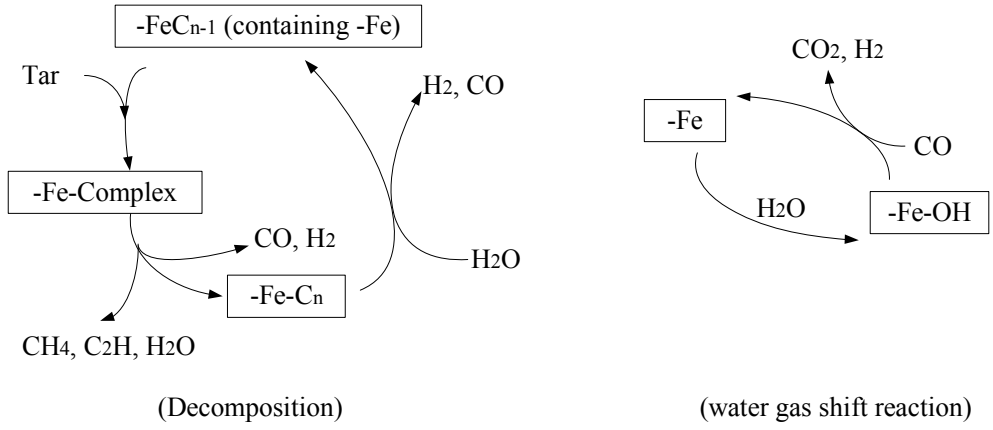

Figure 3. Schematic diagram of mechanism of a catalytic decomposition of tar over iron oxide catalyst.

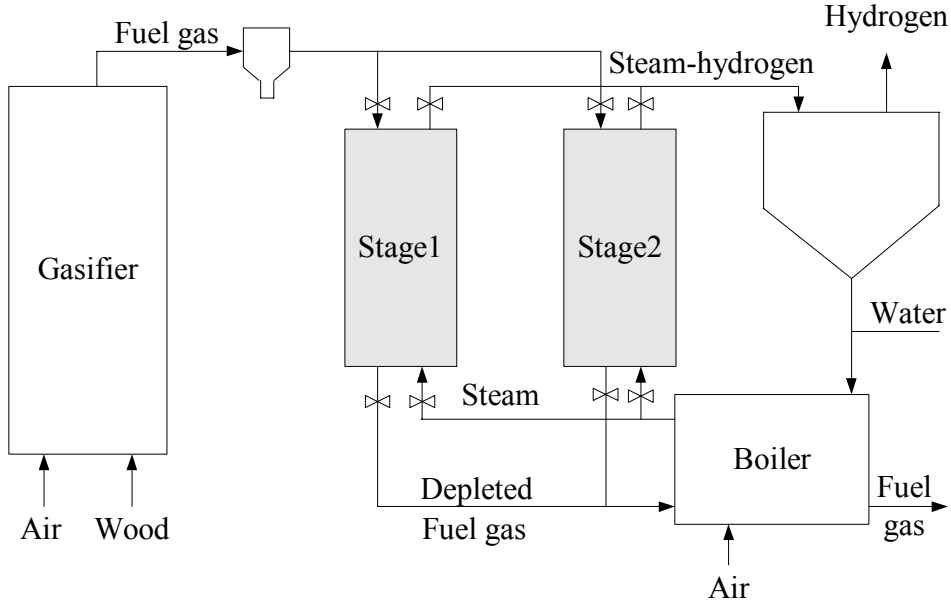

Figure 4. Basic REDOX process diagram.

Fe oxides are good oxygen carrier for redox reaction, and applied by REDOX technology for biomass gasification to produce syngas. Cyclic reduction and oxidation (REDOX) technology was initially developed during the late 19th and early 20th century for the production of hydrogen and CO from coal [28]. The technology was based on cyclic reduction and oxidation of iron oxides. In the first stage the metal oxide material was reduced using fuel gas (Figure 4). The material was then re-oxidized in a second stage by either steam (for hydrogen production) or air (for nitrogen production).

Examples of the relevant chemical equilibrium are:

Stage 1: $Fe_3O_4 + CO + H_2 \longleftrightarrow FeO+CO_2 +H_2O$;
Stage 2: $FeO + H_2O \longleftrightarrow Fe_3O_4 + H_2$

Hydrogen may be made from biomass fuel gas using a method of cyclic reduction and oxidation (REDOX) of iron oxides. Sime [29] simulated REDOX technology to produce of hydrogen by fuel gas. A lab scale REDOX system was developed to provide experimental data. The inherent thermodynamic constraints of the REDOX process limit the maximum efficiency. The REDOX hydrogen process is significantly less efficient and more costly than conventional hydrogen technology.

2.1.2. Ce, Gd Catalysts

Other metals such as Ce, Gd, et al. were also found "mobile oxygen" structure, and were used as an active site or promoter for biomass gasification process.

Miyazawa [30] investigated various oxide supported Ni catalysts in steam gasification. It is found that CeO_2 support played an important role on the decrease of coke deposition [31]. Subsequently, they compared $Ni/CeO_2/Al_2O_3$ catalysts prepared by co-impregnation and impregnation methods in the steam gasification of real biomass (cedar wood). Characterization by means of temperature programmed reduction suggests that the intimate interaction between Ni and CeO_2 on the $Ni/CeO_2/Al_2O_3$ by the co-impregnation method can be related to high performance in steam gasification of biomass.

Zhang [32] found that 3.0% NiO/olivine doped with 1.0% CeO_2 was the most promising catalyst based on catalytic activity and its resistance to coking for tar cracking.

$Gd_{0.1}Ce_{0.9}O_2$ is a material with good catalytic properties for the reduction of tars and has the capability for a redox cycle, but for this, a very low partial pressure of oxygen is necessary [33].

2.2. Perovskite Catalysts

Perovskite is any material with the same type of crystal structure as calcium titanium oxide ($CaTiO_3$, known as the perovskite structure), and shown as Figure 5. They have good catalytic properties towards conversion of hydrocarbons, a high oxygen diffusion coefficient and are able to transport oxygen from the lattice via a redox cycle without changing their crystal structure ($ABO_{3-\delta} \leftrightarrow 1/2\,\delta O_2 + ABO_3$) [34,35]. The amount of available oxygen (δ) is a function of the material composition and the difference of oxygen partial pressure in the redox cycle.

Reactive bed materials for the optimization of the biomass gasification in a fast internally circulating fluidized bed (FICB) reactor system were tested in a micro-scale fluidized bed reactor. Perovskite-type oxides, $Ba_{0.3}Sr_{0.7}Fe_{0.9}Mn_{0.1}O_{3-\delta}$ and $La_{0.65}Sr_{0.35}Cr_{0.5}Mn_{0.5}O_{3-\delta}$, were examined under realistic redox-cycling conditions to study their oxygen capacity and release, their catalytic activity towards toluene reforming as well as their mechanical and chemical stability [33]. The simulated FICFB showed as Figure 6, proposed by Hofbauer et al.[36].

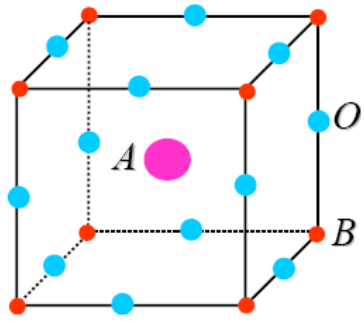

Figure 5. Perovskite structure.

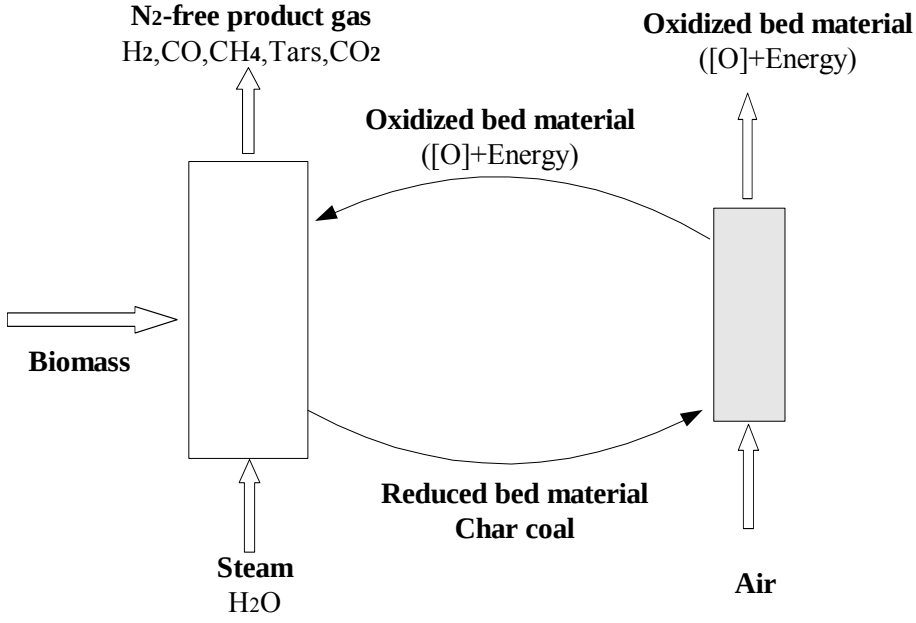

Figure 6. Scheme of a fast internally circulating fluidised bed (FICFB) biomass gasification system as developed by Hofbauer et al (1997).

Tri-metallic perovskite catalysts have been prepared with a sol-gel technique and fully characterized in relation to their structure and reactivity performance [37]. $LaNi_{0.3}Fe_{0.7}O_3$ has been identified as possessing the best activity for the hot gas produced by fluidised-bed steam gasification of biomass materials. No coke formation was observed on the catalyst surface during experimental time.

2.3. Mayenite and Related Catalysts

Mayenite was another catalyst with mobile oxygen in the structure (Figure 7). It has been described previously as a calcium-aluminate framework, in which 32 of the 33 oxygen anions are tightly bound, containing large cages, 1/6 of them being filled randomly by the remaining

"free oxygen" [38,39]. Mayenite ($Ca_{12}Al_{14}O_{33}$) was developed and used in our group, proved that it had high performance on hydrocarbon catalytic combustion because of its high oxygen restored property [40,41].

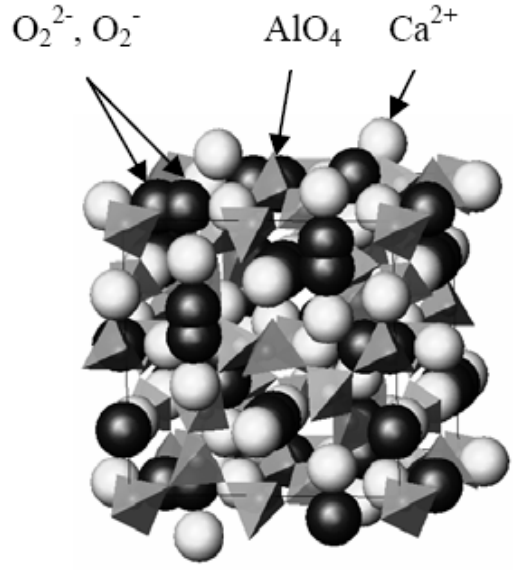

Figure 7. Schematic drawing of mayenite, (Each AlO_4 is three dimensionally linked with one another by sharing corner oxygen atoms. 'free' oxygen is located in micro-pores of mayenite).

Recently, "mayenite" as the nickel support was prepared in our lab, and exhibited excellent performance for biomass tar reforming [42-46]. The special catalyst has higher "mobile oxygen" store ability. If the "mobile oxygen" was consumed in reduced environment, the "mobile oxygen" could restore in oxidation environment. The appearing and disappearing behavior of O_2^{2-} and O_2^- by Raman spectroscopy for fresh mayenite and Ni/mayenite (a), and also for Ni/mayenite (%)after reaction with H_2 or oxygen gas at 650℃, and shown in Figure 8, which includes the fresh mayenite and Ni/mayenite, and also restore ability of Ni/mayenite. The intensity of two Raman bands (880 and 1090 cm^{-1}) of Ni/mayenite decreased after reacted with H_2, and the intensity of two bands in Ni/mayenite was restored after reacted with oxygen. The disappearing and reproducing behavior of molecular oxygen anions of mayenite was also confirmed from TG measurements in our previous study [47], in which the reduce environment was H_2. Reaction with hydrogen decreased the weight of mayenite, and reaction of oxygen restored their weights.

To confirm the practical applicability of the promising industrialization catalyst, long-term durability test was conducted by experiments (800℃, space velocity of 6000h^{-1} at 25□and inlet toluene concentration of 4000ppm, the ratio of steam to carbon in C_7H_8--S/C is 1.15). The results were shown in Figure 9, which illustrated Ni/mayenite maintain more than 98% of toluene reforming for more than 60 hours at 800℃, more stable than that of traditional Ni/Al_2O_3.

Toluene conversion, H_2 yields and the selectivity of CO_2 and CO were calculated with the formula (1-3). Toluene conversion, X_c, can be defined as Eq.1:

$$X_c = \frac{C_{T,in} - C_{T,out}}{C_{T,in}} \times 100 \quad (1)$$

$C_{T,in}$ and $C_{T,out}$: Toluene molar concentration of the inlet and outlet gases.

Hydrogen yield, Y_{H_2} (Eq.2), is expressed as the total conversion of toluene according to the reaction ($C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2$).

$$Y_{H_2}(\%) = \frac{[C_{H_2}]_{out}}{18[C_{T,in} - C_{T,out}]} \times 100 \quad (2)$$

The carbon containing products (CO, CO_2) are calculated by the selectivity S_i (Eq.3).

$$S_i = \frac{[C_i]_{out}}{7[C_{T,in} - C_{T,out}]} \times 100 \quad (3)$$

[C_i]: molar concentration of i =CO, CO_2

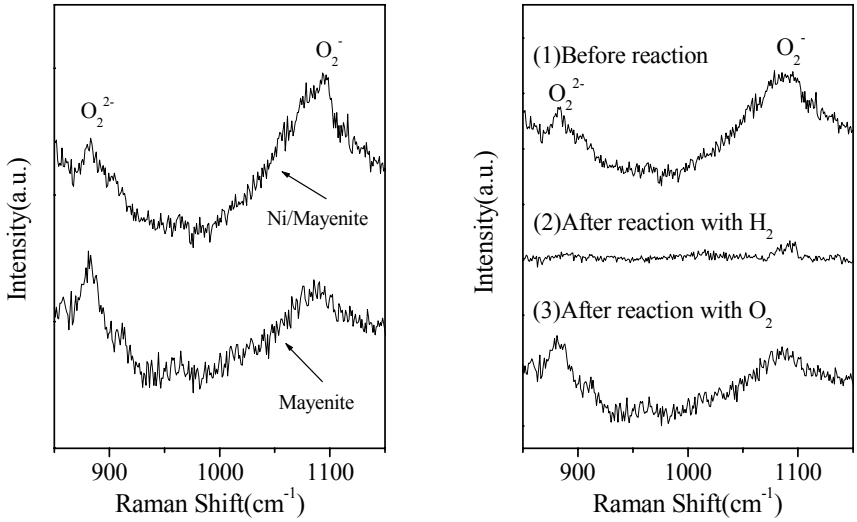

Figure 8. Raman spectra of mayenite and Ni/mayenite before reaction.

By analysis, at least three possible reasons to account for such unexpected observation may be considered. The first possibility is that the excess S/C ratio can prevent or reduce the formation of coke on the catalyst, especially the ratio above 1.2 [48], but the long-time evaluation of our experiments was carried out on the smaller S/C (1.15). A second possibility is that the formation of coke deposits on the surface of mayenite not of nickel metal. In some cases, most of the formation of coke deposited on the supported surface, but only small

amount on the activity component surface [49]. The quantitative analysis of coke amount on the after reaction catalyst performed with the TG analyzer (TGA, Rigaku Thermo Plus TG8120). The sample of 50-70mg was heated from 30 to 1000℃ with a heating rate of 10 ℃/min in air. The weight loss convincingly due to the combustion of deposited carbon less than 0.1% was observed, which indicated nearly no carbon deposition on Ni/mayenite. So the third possibility is the "free" oxygen in the special structure of mayenite (Figure 7), which was attributed to the presence of hydroxide, peroxide and superoxide radicals in the cages.

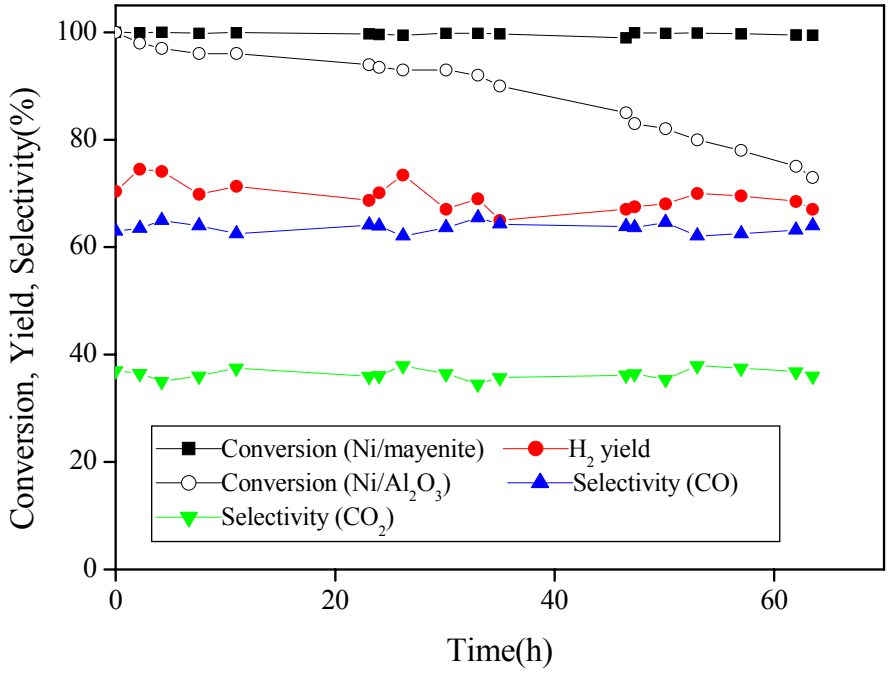

Figure 9. Toluene conversion, H_2 yield, CO and CO_2 selectivity vs time, (S/C=1.15, temp=800℃, toluene concentration=4000ppm).

Beside this, the catalyst also exhibit excellent sulfur-tolerant property, the "mobile oxygen" can be substituted by "S" atom, then protect Ni poison.

The simulated biomass gasification sulfur containing for catalyst deactivation testing had following composition: toluene 4000ppm, diluted by H_2S/Ar (H_2S: 500ppm), appropriate steam was filled by syringe, At this condition, the model compound toluene and H_2S with a concentration of 4000ppm and 500ppm respectively was rather serious condition for biomass gasification gas.

The effect of H_2S on the performance over Ni/mayenite (3 and 5%) was studied, and the results were compared to that of Ni/50CaO/50Mg (5%) and Ni/Al_2O_3 (5%). The catalytic performance as a function of time was shown in Figure 10. The activation decreased gradually and quickly for the Ni/Al_2O_3 (5%) and Ni/50CaO/50Mg (5%) respectively, but for Ni/mayenite, the activation could be divided into two stages, under this reaction condition (H_2S: 500ppm, the space velocity: 6000h^{-1}), for the initial 60min stage, the conversion and the

products were similar with that of the absence of H_2S, but after this period, the toluene conversion decreased quickly, then still kept constant.

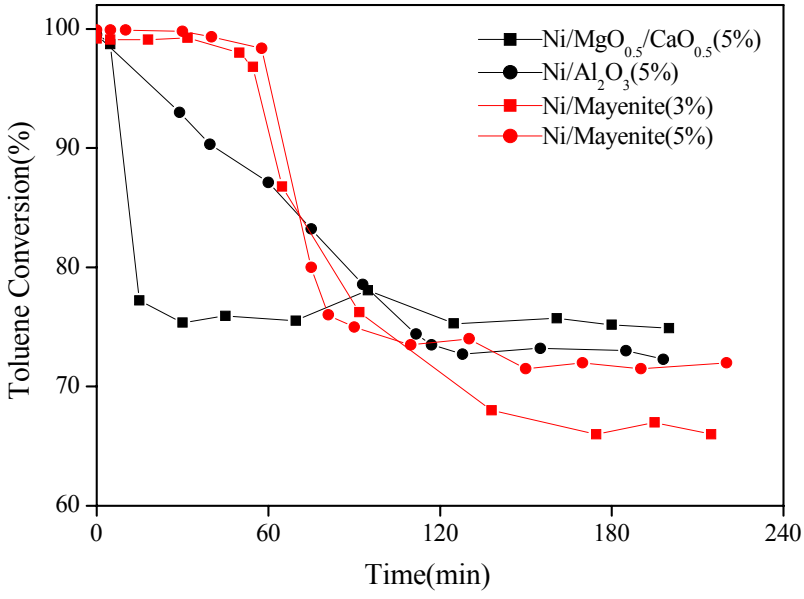

Figure 10. Toluene conversion vs. time on different catalysts, (H_2S: 500ppm, S.V.: 6000 h^{-1}, Temp: 800℃).

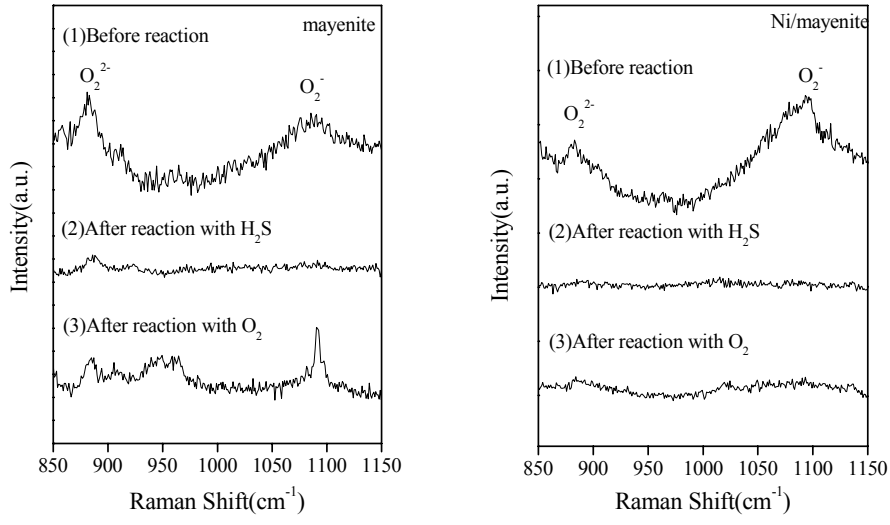

Figure 11 Raman spectra of mayenite (a) and Ni/mayenite (b) after reaction with H_2S or oxygen gas at 650℃.

By analysis, the reasonable possibility to account for such unexpected observation is the "free" oxygen in the special structure of Ni/mayenite, in which mayenite can absorb sulfur, and protect Ni metal, then prolong the life time.

But from the results of our experiments, the sulfide catalyst by H_2S was hardly restored, and the sulfide mayenite was more stable than mayenite. The appearing and disappearing behavior of O_2^{2-} and O_2^- was examined by Raman spectroscopy after reaction with H_2S or oxygen gas at 650℃. Figure 11 shows the results of mayenite (a) and Ni/mayenite (b). The intensity of two Raman bands (880 and 1090 cm^{-1}) of the mayenite and Ni/mayenite decreased after reacted with H_2S, and the intensity of two bands in mayenite was partly restored after reacted with oxygen, but this was not obvious for Ni/mayenite. Between these two species, O_2^- was more preferentially consumed under a H_2S atmosphere. The disappearing and reproducing behavior of molecular oxygen anions of mayenite was also confirmed from TG measurements in our previous study [47], in which the reduce environment was H_2. Reaction with hydrogen decreased the weight of mayenite, and reaction of oxygen restored their weights.

CONCLUSION

View the past research, "mobile oxygen" catalysts exhibited special performance in biomass gasification process, such as anti-carbon formation, improving sulfur toleration and so on. The development and application of these kinds of catalysts such as the low-cost metal Fe, simple perovskite and so on are attracting more research and focus. Research on the mechanism of the reactions is still imperative. These catalysts may be lead to reduction in the biomass gasification process.

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Chapter 11

BIOMASS PRODUCTION WITH FAST-GROWING TREES ON AGRICULTURAL LAND IN COOL-TEMPERATE REGIONS: POSSIBILITIES, LIMITATIONS, CHALLENGES

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ABSTRACT

High density plantations of fast-growing tree species grown on fertile land are today a viable alternative for the production of bio-fuels in many countries of cool-temperate regions. For example in Sweden, willow biomass plantations are commercially grown for energy purpose. Rapid development of sustainable production systems and infrastructure, along with recent progress in tree crop breeding resulted in high biomass production potential on fertile agricultural land. In addition, tree plantations can increase biodiversity in open agricultural landscapes and serve as tools for the amelioration of environmental problems at local (e.g., waste product contamination through phytoremediation) and global scale (e.g. increased greenhouse effect through carbon sequestration). Thus, multifunctional biomass plantations offer additional possibilities in terms of, e.g., wastewater cleaning and carbon sequestration. However, the establishment and large-scale implementation of woody biomass plantations is often controversial due to, for example, presumed negative influences on biodiversity and the cultural heritage landscape, along with negative public attitudes. Conflicting interests of different parts of society and socio-political issues (e.g. agricultural and energy policy, market developments, public attitudes) are therefore major barriers for the rapid development of woody bio-fuel plantations in Sweden and many other countries, rather than climatic, technical or environmental constraints. In future, careful analysis of the non-technical, non-climatic barriers at regional level and possibly the development of guidelines for the establishment and sustainable, environmentally friendly management of woody biomass

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plantations could be means to boost the utilization of woody biomass from agricultural land in many countries of the world.

INTRODUCTION

High density plantations of fast-growing tree species, grown in single stem or coppice systems and producing woody biomass, are today a viable alternative to food production on agricultural land (c.f. reviews by Mitchell et al. 1992; Zsuffa et al. 1993; Makeschin 1999). The biomass produced is used for pulp and paper industries as well as energy purposes, but also as construction wood or fodder. Compared with traditional forest trees such as spruce or pine, the species used (e.g., eucalypts, poplars, aspens and willows) have a number of biological characteristics in common which make them amendable to intensive culture, i.e., high productivity rates particularly during the first years after planting, high photosynthetic capacity in combination with large leaf areas and high allocation of biomass to harvestable stem wood in relation to root and leaf biomass (e.g., Cannell et al. 1988; Ceulemans et al. 1996). The establishment of plantations of fast-growing trees has more in common with agricultural crops than forestry. Ground preparation is carried out using conventional agricultural machinery and methods. In general, the crop is planted by simply pushing stem cuttings into the cultivated soil. Shoots and roots quickly develop from these cuttings. The developing shoots are left to grow on for between 2 and 4 years (coppice systems) or 10 to 20 years (single tree systems) before being harvested with specialised machinery (Figure 1). In the case of coppice systems, the stump of each stool is left in the ground and produces more shoots that grow for a further 2 to 4 years until the next harvest. Several 2- to 4-year cutting cycles can take place in coppice systems before yield declines and the crop needs to be replaced.

Especially when grown for energy purposes, intensively managed plantations of fast-growing trees on agricultural land are gaining increasing interest in many countries of the world, due to their efficient and sustainable land use in combination with an increasing demand for renewable energy sources (Volk et al. 2004) and the additional possibilities for environmental control (phytoremediation, Crites 1984; Aronsson and Perttu 2001). For example, life cycle analysis of willow biomass production on agricultural land based on commercial clones and cultivation practices in Sweden revealed high energy efficiency of the production system: The produced biomass yields 20 times more energy compared to the energy input, a figure which is more than 3 times higher than the energy balance (i.e., energy output / energy input) of annual energy crops such as wheat and rape (Börjesson 2006). In addition, plantations of fast-growing trees require a reduced chemical input when compared to conventional arable crops, can provide an alternative use of agricultural land and can enhance the local environment through increased biodiversity. Thus, agricultural land cropped with fast-growing trees can become an important supplier of energy with marginal contribution to the increasing quantity of greenhouse gases in the atmosphere. These plantations can sequester large amounts of carbon (for *Salix* see Grogan and Matthews 2002) and may have a great potential to contribute to carbon-managed future economies in terms of fossil fuel replacement and carbon sequestration (Hall and House 1994; Tuskan and Walsh 2001).

Figure 1. Combined harvest and chipping of 3-year old shoots in a 7-year old Salix stand near Enköping, Central Sweden. Harvest is performed during winter when the ground is frozen and the plants are dormant. Photo: P. Aronsson.

The greatest potential for high biomass yields with fast-growing trees is commonly assumed in areas with warm and humid climatic conditions supporting rapid plant growth, e.g., the warm-temperate and sub-tropical climate. The most common tree species used under these climate conditions are eucalypts and poplars, for which adequate production systems have been developed (e.g., in central and southern Europe, North America, Australasia, Brasilia). But also cool-temperate and boreal floras hold fast-growing tree species that are suitable for intensively managed fast-wood plantations in high-latitude regions. Thus, adequate production systems were developed also for boreal regions (Weih 2004).

In Sweden, for example, a production system for the commercial production of biomass from intensively managed willow has been developed in the frame of a National Energy Forestry Programme and currently willow plantations for energy purpose cover an area of more than 16 000 ha in Sweden. However, intensive willow culture has raised concerns about environmental, biodiversity and landscape design issues, and there are risks for conflicts between the interests of commercial willow growers and, e.g., environmentalists. In this chapter, an overview of the development of a biomass production system based on willow will be followed by a discussion of environmental and landscape design issues. Further, an analysis of potential synergies and conflicts between the objectives of commercial willow culture, nature conservation and landscape design will be presented.

DEVELOPMENT OF COMMERCIAL BIOMASS PRODUCTION BASED ON WILLOWS IN SWEDEN

Willows (genus *Salix*) are part of the natural flora in temperate-arctic regions and products from willows have been used traditionally in Sweden. The cultivation of willows (basket making, fencing, etc.) was performed at a rather small scale until relatively recently,

when the potential of willow as bioenergy crop came into focus. Today Sweden is one of the few countries in the world where willow cultivation exceeds poplar growing.

In Sweden, research on willows for the purpose of biomass production was firstly initiated in the late 1960s in response to a predicted shortage of raw material for the pulp and paper industry. The energy crisis in the early 1970s supplied further arguments for the development of national energy systems that are not based on fossil fuels. In addition, the existence of many district heating systems in Sweden favored the large-scale utilization of woody biomass (Hoffmann and Weih 2005). Thus, in Sweden, willow cultivation as a source of biomass for energy purpose has been developed within the frame of a National Energy Forestry Programme (Sirén et al. 1987, Christersson et al. 1993) and expanded from a few hectares around 1970 to about 16 000 ha by the end of the 1990s. An increase to about 200 000 ha, which corresponds to almost 10 % of the agricultural land in Sweden, is envisaged during the next 15 years (Energimyndigheten 2001).

The research and development of willow culture in Sweden involved many research groups dealing with all aspects of willow genetics, physiology and ecology. The majority of research on the willow production system was done at the Swedish University of Agricultural Sciences (SLU). For example, the typical design of the willow production system in densely-spaced double-rows was developed at the SLU (Sirén et al. 1987, Christersson et al. 1993) and the research resulted in the publication of management guidelines for practical willow culture on agricultural land (e.g., Danfors et al. 1998). Also nature conservation aspects were addressed along with the development of the willow production system (Gustafsson 1987, Aronsson 1995). The plant material used for the first willow trials often performed poorly in terms of growth rate and frost tolerance. A country-wide campaign in 1978 resulted in 190 *Salix* varieties with annual shoots longer than 2.5 m (Sennerby-Forsse et al. 1983). New collections have been made since then and the clone archive at the SLU today holds about 600 different varieties of *Salix*. Based on these collections and early breeding work by G. Sirén, breeding programs for *Salix* with the aim of increasing biomass production by phenotypic screening and recurrent selection have been initiated at the SLU (Gullberg, 1993). As a result, genetic linkage maps are now available for *Salix* (Rönnberg-Wästljung 2001, Tsarouhas et al. 2002, Rönnberg-Wästljung et al. 2003).

The research and development of willow culture in Sweden was accompanied by commercialization of both production system and breeding. Thus, most commercial willow plantations in Sweden are today administrated by the Federation of the Swedish Farmers Coops, through the company Agrobränsle AB located in central Sweden (Larsson et al. 1998). This enterprise has contacts with subcontractors and utility operators and guarantees the proper handling of the crop through advisory service. Agrobränsle AB takes also care of harvest and delivery of the willow wood chips to the closest district heating plant.

Species of *Salix*, as well as closely related *Populus*, are characterized by high initial growth rate, but relatively short life time; easy vegetative propagation (stem cuttings; e.g. willows) and/or formation of coppice sprouts or suckers (e.g. aspens); relatively early flowering; small genome size; and light wood that is uniform in texture and used by industry and for energy (e.g. Dickmann 2001, Verwijst 2001). Easy propagation, early flowering and small genome size are all characteristics that facilitate rapid improvements by means of breeding efforts and make willows and poplars very interesting for plant breeders (Taylor 2002, Wullschleger et al. 2002).

A major characteristic of production systems based on fast-growing trees is a very rapid achievement of maximum production figures already after few years (e.g., Weih 2004): biomass production rates (mean annual increment, MAI) of > 20 Mg ha^{-1} $year^{-1}$ were achieved after 3 to 5 years in fertilized (experimental) willow stands grown in Sweden and Canada (Christersson 1986, Labrecque and Teodorescu 2003). However, such high production figures have been achieved only in small-scale experimental plantations and biomass yields in commercial willow plantations grown in southern and central Sweden are usually in the range 5 to 10 Mg ha^{-1} $year^{-1}$.

The fertilization with mineral nutrients is normally necessary to ensure sufficiently high biomass yields for the economically sound culture of fast-growing trees such as willows, especially when grown under cool-temperate climate (Weih 2004). In Sweden, the use of nutrient-rich residues as an alternative, cost-efficient fertilization method was developed in parallel with the development of appropriate production systems for willow culture as a source of biomass for energy purpose (Perttu 1993, Aronsson and Perttu 2001). The principal residues used in Sweden are urban wastewater, landfill leachate, log-yard runoff, sewage sludge and wood-ash and the benefits are both environmental and economic (Dimitriou and Aronsson 2005).

ENVIRONMENTAL CONCERNS, BIODIVERSITY AND LANDSCAPE DESIGN

During recent years the planting of large areas of fast-growing trees has sparked off much controversy, especially in the areas of the world where most of the expansion of fast-wood plantations is expected to take place (i.e., South America and East Asia). Critics of these plantations of fast-growing trees include environmentalists, who argue that they are causing harm to wildlife, water resources and the soil and decrease biodiversity (Cossalter and Pye-Smith 2003). Indeed, much tree planting in recent decades, especially in the Tropics, has had negative environmental impacts, but the problems of plantation forests are frequently associated with inappropriate location and management; therefore, relatively modest changes in the ways that tree plantations are established and managed could result in greatly improved outcomes for the environment (WWF 2003). Thus, the localization and management of plantations of fast-growing trees should be planned carefully, in order to reduce the risks for environment and utilise at best their potential to improve environmental and landscape quality. For example, intensively managed plantations of fast-growing trees imply the risk of negative effects on the environment in terms of herbicide application, deteriorated soil properties and nutrient leakage. However, when compared to conventional arable crops, the perennial character of the crops used in tree plantations commonly leads to reduced herbicide application (i.e., herbicide treatment is required only during the establishment of the crop). Further, afforestation with fast-growing trees on former arable land has often positive effects on soil properties due to less frequent use of heavy machinery, especially when the use of harvesters is restricted to the period of frozen ground in winter-cold regions. For example, carbon sequestration and water holding capacity were found to increase in formerly arable soils that were planted with fast-growing willow and poplar for 6 to 10 years (Kahle et al. 2005). The perennial nature of tree plantations also leads to less nutrient leakage compared to

conventional arable crops provided that the rate and timing of fertilization is adjusted to the nutrient delivery and nutrient holding capacity of the soil in relation to the uptake capacity of the trees (Ericsson et al. 1992). This may imply the application of repeated, small fertilizations throughout the growing season according to a scenario following tree growth, i.e., small amounts early and late in the season and larger amounts in mid-summer (Ingestad 1987, Alriksson et al. 1997). Particularly in plantations with wider tree spacing grown in single-tree systems (e.g., poplars and eucalypts), nutrient supply by placing close to the roots of individual trees is an option to prevent leakage to groundwater (van den Driessche 1999). If tree plantations are managed according to these principles, they are unlikely to endanger the environment by means of groundwater contamination even under the short periods of plant nutrient uptake that are typical under the cool climate of high-latitude regions (Aronsson et al. 2000).

In contrast to the potential risks of nutrient leakage from fertilized plantations, plantations of fast-growing trees can offer great possibilities for environmental control at a local scale in terms of, e.g., phytoremediation. Thus, based on the large nutrient quantities taken up by fast-growing trees, the plantations can be used as recipients for municipal wastewater and industrial sludge and simultaneous biomass production (multifunctional biomass plantations, Perttu 1993, Isebrands and Karnosky 2001, Aronsson and Perttu 2001, Labrecque and Teodorescu 2003). A major problem occurs particularly in regions with extended dormant periods during winter, where only very small quantities of nutrients are taken up by plants. This sort of wastewater treatment can therefore be accomplished in winter-cold regions only if the wastewater is stored in ponds or lagoons during the winter period (Rosenqvist et al. 1997).

Tree plantations can have positive or negative effects on biodiversity, depending on location, management and previous land use (Cossalter and Pye-Smith 2003) and studies on biodiversity in plantations of fast-growing trees often arrive at contradictory conclusions especially when different kinds of organisms are considered (Hartley 2002). Thus, the landscape context (forest or agricultural, Hanowski et al. 1997, Weih et al. 2003) along with the land-use type that the plantation replaces (Christian et al. 1994) and spatial scale aspects (e.g. size or shape of plantation; Christian et al. 1994, Berg 2002) influence the impact of establishment of tree plantations on biodiversity. In addition, many animals use multiple habitats and therefore depend on certain habitat combinations (With et al. 1997, Law and Dickman 1998) and the diversity of land use types in a given landscape can have large impacts on biodiversity.

Compared to natural mixed coniferous forests of the Pacific Northwest, Halpern and Spiess (1995) regarded large poplar plantations to decrease flora diversity in the long term. In comparison to managed coniferous forests and farmland in boreal Sweden, young poplar and willow plantations have however been concluded to increase vascular-plant diversity (Figure 2; Gustafsson 1987, Weih et al. 2003, Augustson et al. 2006).

Similar to the observations on floras, fauna diversity (birds and mammals) is frequently found to be higher in willow and hybrid poplar stands compared to agricultural croplands (Christian et al. 1998, Berg 2002). Thus, the more extensive management of tree plantations compared to intensively managed cereal crops can improve habitat quality for many organisms including plants, birds and arachnids (Berg 2002, Blick and Burger 2002, Dhondt and Wrege 2003, Weih et al. 2003).

Figure 2. July aspect inside a 2-year old Salix stand grown on the island Gotland, south-eastern Sweden. Small-scale plantations of fast-growing trees can enhance biodiversity at landscape-scale. Photo: M. Weih.

In addition, plantations of fast-growing trees appear to have a potential as important habitats for gamebirds (Sage and Robertson 1994). The location of tree plantations within the landscape context exerts a strong influence on their effect on biodiversity: A native wood nearby the tree plantation will facilitate the migration of birds, insects and plants and, thus, increase biodiversity. If no native woods are present, small groups of native trees can be planted nearby the fast-wood plantation. The native woods will serve as retreat area where animals and insects can survive during the periods of clear-cut in the fast-wood plantation. In large plantations, different parcels of the stand can be established and harvested in different years in order to enhance structural diversity and biodiversity. The same goal could be achieved by establishing a large number of smaller plantations, which are harvested in different years. Both alternatives can possibly improve the possibilities for biological control of herbivorous insects, which can be a serious problem in fast-wood plantations (Björkman et al. 2004). Mixtures of different species or varieties can be established either by planting them in different blocks across the field or random mixtures within each row (e.g., Aronsson 1995, Volk et al. 2004). These mixtures increase structural and functional diversity and contribute to reduce the impact of pests and diseases (Ramstedt 1999, McCracken and Dawson 2001). Finally, a few meters wide stripes along the edges of tree plantations could be left without trees to support the development of a rich native flora and fauna.

It hence appears that intensively managed tree plantations, if not to large in size and if planned creatively, can increase the abundance and diversity of many organisms, particularly in landscapes dominated by either conventional agricultural fields or managed coniferous forests, by increasing structural diversity. However, plantations should be avoided close to open habitats of high conservation values such as certain types of wet meadows and buffer zones along streams, because such sites often have a conservation value linked to openness of the habitat (Berg 2002). With the above restrictions in mind, small-scale tree plantations (or

sub-divided larger plantations) grown on agricultural land may have the potential to positively affect biodiversity in many farmland regions, where the set-aside of agricultural land from food production suggests the development of alternative uses.

Plantations of fast-growing trees may already after few years of growth be up to 6 or 8 m in height and it is important to consider the impact this will have on the landscape at the early planning stages of a fast-wood plantation. Many concerns are raised regarding the impact of plantations of fast-growing trees on the landscape (e.g., Skärbäck and Becht 2005): Will the open agricultural landscape be "darkened" by a new type of forest? How will the new crop be adapted to the traditional field crops of agricultural landscapes? Will we soon experience a total transformation of our ingrained cultural heritage? Studies regarding the effects of plantations of fast-growing trees on visual landscape perception usually arrive at different conclusions, e.g., the more open the landscape is, the larger can the size of the plantations be and particularly small plantations placed in open agricultural landscape can enrich landscape perception; small-scale undulating landscape only "tolerates" small plantations (Rode 2005, Skärbäck and Becht 2005). A general comment is often that plantations of fast-growing trees are an exciting new feature of the landscape, these plantations can enhance the aesthetic value of landscape by adding variation (e.g., autumn colors; Figure 3) and structure in homogeneous agricultural landscape (Skärbäck and Becht 2005). If used creatively as part of active landscape analysis and design, plantations of fast-growing trees can greatly improve the visual and recreational values of a landscape (e.g., Enberg 2002, Rode 2005). For example, monotonous structures in blocks of tree plantations can be broken up by edge stripes of native herbs and woods, which are flowering and thereby can increase the aesthetic value of the landscape (Rode 2005).

Figure 3. Variation of autumn colours in 1-year old shoots of different Salix varieties grown in a plantation near Uppsala, Central Sweden. Cultures of fast-growing trees can increase the aesthetic value of landscape, particularly if different varieties are planted. Photo: N-E. Nordh.

Concerns have also been raised regarding the impact that plantations of fast-growing trees might have on archeological sites and deposits. However, these plantations will be no more damaging to archaeology than arable cropping or commercial forestry and most critical

sites such as very wet profiles are not desirable for the establishment of fast-growing trees even by other (biological) reasons. Particular attention should nevertheless be paid to the potential impact of plantations of fast-growing trees on the conservation of historic, designed landscape and it is important to consider these aspects at the early planning stages of this kind of plantation.

SYNERGIES AND CONFLICTS OF INTERESTS

Plantations of fast-growing trees are economic enterprises in most cases and economic profit arguments (i.e., maximised biomass yield after shortest possible time) usually guide their localization, shape and management in the first place. Localization, shape and management of commercial fast-wood plantations are partly conflicting with the primary interests of nature conservation and landscape design (Table 1). Regarding localization of fast-wood plantations, no serious conflicts of interest appear to exist between the interests of commercial growers, nature conservationists and landscape designers (Table 2) if plantations are established outside areas of high nature conservation and cultural heritage values. Synergies between commercial and nature conservational interests could be achieved by localization of plantations nearby native woods, which favour biodiversity (see above) and also shelter the plantation from extremes in climate (e.g., frost) and, thereby, improve sustainable productivity of the plantation (Weih 2006). No serious conflicts of interests are expected between nature conservation and landscape design principles of shaping and managing tree plantations (Tables 1, 2). Possibly could synergies be achieved through the establishment of edge habitats consisting of attractive (flowering) plants that have high conservational value for plants and insects.

Commercial willow culture may frequently conflict with the interests of nature conservation and landscape design regarding the shape and management of tree plantations. For example, large monoclonal, block-shaped and very fast growing tree stands that are harvested frequently as a whole are desirable from a purely commercial perspective, whereas many small-sized, unregularly shaped stands consisting of several species and/or clones and harvested in different years would be preferred by nature conservationists and landscape designers (Tables 1, 2). An active dialogue between commercial *Salix* growers, nature conservationists and landscape designers will facilitate feasible compromises between the conflicting interests.

Misconceptions and a lack of knowledge on intensive tree culture and its effects on environment and landscape are among the most common non-technical barriers for the full-scale implementation and dissemination of plantations of fast-growing trees in Sweden and other countries (IEA 2005, Weih 2006). Lack of correct information, ignorance of best-practice advice (Helby et al. 2006) and misconceptions often generate negative public attitudes and biased decisions of authorities that are directly or indirectly involved in the formal regulation process regarding these plantations (Weih 2006). There is indeed a large body of knowledge available since many years on how fast-wood plantations should be localized and managed in order to favor environmental and landscape qualities (e.g., Aronsson 1995, DEFRA 2002, Volk et al. 2004). However, this knowledge is rarely applied in commercial plantations of fast-growing trees.

Table 1. Desirable actions for localization, shape and management of plantations of fast-growing trees according to purely commercial, environmental (nature conservation) and landscape design principles (after Weih 2006)

	Commercial	Nature conservation	Landscape design
Localization	Agricultural land, short transport distances to end user, easy accessibility with heavy machinery	Agricultural land, nearby native woods, not in areas of high nature conservation value and not in landscape dominated by forest	Not in areas of high cultural heritage value and at visually exposed locations where traditional landscape views would be destroyed, preferably in open and homogeneous agricultural landscape, not in areas dominated by forest (to prevent a negative perception of landscape, the total fraction of forested area in a landscape should not exceed 40 - 50%, Wöbse 2003)
Shape	Large and block-shaped plantations that can be harvested effectively, homogeneous and highly productive plant material (preferably monoclonal stands) that rapidly generates homogeneous biomass	Small-scale plantations, stripes or small groups of native woods in the edges of the plantation, heterogeneous plant material (preferably multi-species or polyclonal stands) including male-sex varieties (insect pollination!)	Small-scale plantations, stripes of native vegetation consisting of attractive species (flowering, autumn colors, etc.)
Management	Effective weeding (chemical) prior to plantation establishment, optimal mineral nutrient fertilization ”according to plant demand” (preferably with sludge or waste water from sewage plant), short cutting cycles, simultaneous harvest of the whole stand	Restrictive application of chemical weeding, not to high nutrient fertilization ”according to plant demand” (to prevent leakage to groundwater), long cutting cycles, different parts of plantation are harvested different years, native edge habitats are left untouched at least during harvest of the tree plantation	No deep ploughing (to prevent disturbance of archeological deposits), native edge habitats are left untouched at least during harvest of the tree plantation

Table 2. Summary of possible conflicts of interest (yes, no) between commercial (C), environmental (nature conservation, N) and landscape design (L) principles with regard to the localization, shape and management of plantations of fast-growing trees grown on agricultural land (after Weih 2006)

	Localization		Shape		Management	
	N	L	N	L	N	L
C	No	no	yes	yes	yes	yes
N		no		no		no

Campaigns and guidelines to disseminate valid information on fast-wood culture and its effects on the environment to authorities and the public, as well as improved communication among authorities, will help to remedy misconceptions and lack of correct information.

The above section has shown that there are potential negative impacts from commercial fast-wood plantations on environment and landscape, but these may be controlled and minimised by application of a creative and integrated attitude to ensure that establishment and management of fast-wood plantations operate in an optimal way to secure the positive impacts on rural economic activity, nature conservation (biodiversity) and cultural heritage.

CONCLUSION

Plantations of fast-growing trees *(Salix, Populus)* offer great possibilities for the efficient use of agricultural land in cool-temperate regions. If the biomass produced is used as bio-fuel, the plantations have a great potential to contribute to carbon managed future economies, because they contribute only marginally to the production of atmospheric greenhouse gases. By combining biomass production and phytoremediation in tree plantations, waste products from society (waste water, sludge, ash) can be used as resources to improve tree growth and generate added values in terms of both environment and economy. Plantations of fast-growing trees grown on agricultural land can improve biodiversity at landscape level, in particular if the plantations are established instead of cultures of cereals and spruce or fallow ground in homogeneous agricultural landscape. These tree plantations can also positively affect soil properties compared to conventional agriculture. Particularly plantations of relatively small size offer great possibilities for landscape design, because they are an exciting new feature in most regions and can enhance the aesthetic value of landscape by adding variation and structure.

Limitations for the localization, shape and management of fast-growing tree plantations are set by economic constraints, the landscape context and by environmental concerns. Regarding the localization of plantations, no serious conflicts between commercial and environmental interests are expected if the plantations are planned outside areas of high nature or culture conservation value. Synergy effects are possible if plantations are located nearby native woods. With respect to plantation management, the commercial practice of intensive tree culture might frequently conflict with the interests of nature and culture conservationists. An active dialogue between commercial growers and nature/culture conservationists will facilitate feasible compromises between the two sides.

Major barriers for the full-scale implementation and dissemination of fast-wood plantations in cool-temperate regions are non-technical, such as lack of correct information and misconceptions in the public and at regulating authorities. A major challenge for the future is to remove these barriers, along with improvement of the plant material used in the plantations.

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Chapter 12

PRODUCER GAS AND VEGETABLE OILS OPERATED COMPRESSION IGNITION ENGINES FOR RURAL APPLICATIONS

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ABSTRACT

Biomass gasification technology emerged during the industrial revolution was successfully used in automobiles, public place lighting, urban household cooking and power generation during the second world war mainly in European countries. The developing countries richer in biomass resources and caught in the rising prices of fossil fuels have again shown interest in biomass technology. India being single largest user of biomass resources finds application in cooking and other house hold purposes. It may be noted that the conversion efficiency with biomass is very low (10 %) as against 80 % in boilers. Biomass combustion in traditional devices produces smoke, carbon monoxide and other health-damaging emissions. Therefore gasification technology requires using biomass resources more efficiently and in a cleaner manner. Judicious use of biomass gasification technology results in savings in fuel wood, furnace oil, diesel, LPG with implications of increased energy security.

Few attempts have been made to popularize biomass gasifiers on a commercial scale. The main reason is the wide spread availability of petroleum based fuels at low prices. Gasifier systems for hot water in hotels, midday meals, cremation, drying rubber, sericulture, tobacco curing are some of the applications wherein biomass technology comes handy. India being predominantly agricultural country requires major attention for the fulfillment of energy demands of a farmer. The increased use of diesel in agriculture and transportation sectors has resulted in diesel crisis. Finding an alternative fuel for

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diesel fuel is critically important for our nation's economy and security. Producer gas from different biomass resources can act as a promising alternative fuel, especially for diesel engines by substituting considerable amount of diesel oil. Use of wood gasifiers to drive engines in single fuel mode of operation has the advantage of having complete independence from petroleum fuels. This feature is very convenient for electricity generation in more remote areas or areas inaccessible for long periods over the year. Further, compared to gasoline engines exhaust emissions like nitrogen oxides (NOx) and (hydro carbon) HC are lesser for producer gas operated gas engines. From derating and fuel flexibility point of view, dual fuel engines are highly acceptable. Modification of existing diesel engine for dual fuel operation with producer gas is simple and power derating is limited to 20–30%. Diesel savings up to 70–90% have been reported for dual fuelling. The lower running cost and the use of alternative fuel sources with dual fuel engine operation has attracted many investigators to apply this type of engine in different areas. The main aspiration from the usage of dual fuel engine is mainly to reduce particulate emissions and nitrogen oxides. It is difficult to simultaneously reduce NOx and smoke in normal diesel engines due to the trade-off curve between NOx and smoke. One prospective method to solve this problem is to use oxygenated alternative fuels to provide more oxygen during combustion.

The present work is an effort to evaluate feasibility of popular alternative fuels in the form of non edible oils of Honge, Rice bran and Neem that are locally available and producer gas as a total replacement for fossil fuels. Experiments have been conducted on a single cylinder four-stroke compression ignition (CI) engine operated on single and dual fuel modes at injection timings of 19, 23 and 27^0 BTDC respectively and injection pressures varied from 205 and 280 bar. Earlier, in single fuel mode of operation, optimum conditions in terms of injection timings and injection pressures for Honge, Rice bran and Neem oils were determined.

Brake thermal efficiency in dual fuel mode of operation is lesser than single fuel mode of operation at all the injection timings investigated. However, it improved marginally when the injection timing was advanced for all the non edible oils tested. The smoke emission for producer gas–non edible oil combinations was found to be more than producer gas–diesel oil. The higher viscosity of non edible oils resulted in poor atomization and mixture preparation with air resulting in higher smoke. With dual fuel operation, smoke and NOx emissions were considerably reduced with increase in (corbon monoxide) CO emissions.

Keywords: Biomass Gasification, Honge oil, Rice Bran oil, Neem oil, injection pressure, injection timing.

1. INTRODUCTION

The environment is greatly polluted by emissions such as CO, CO_2, NO_x, SO_x, unburnt or partially burnt HC, and particulate from transport vehicles. The chief contributors to urban air pollution and major source of green house gases are fossil fuels, and they are considered to be the major cause for the global warming. Petroleum fuel reserves are fast depleting in nature, and the cost of crude petroleum is sky rocketing and is presently $140 per barrel (2008). World petroleum consumption was 1.5 million bbl/d (768 trillion dollars/day) in 2007. India's current monthly oil import averages are at $7.7 billion (Rs 33,000 crore) and at this rate our annual oil import bill will reach $112 billion (Rs 470,000* crore). In view of this high

demand and cost of fossil fuels associated with higher emissions, it is necessary to find suitable alternative to diesel oil. Hence research is focused on the use of vegetable oils as an alternative fuel since it is renewable, non-toxic, biodegradable, and have low emission profiles [1-15]. There is an increasing interest in many other countries as well to search for suitable alternative fuels that are locally available and environment friendly too. Vegetable oils and their methyl esters are such alternative renewable fuels for compression ignition engines.

Inherent properties of vegetable oils make them suitable for use in diesel engines solely with an acceptable loss in efficiency. There are two types of vegetable oils derived namely edible oil and no-edible oils. Non-edible oils such as Honge, Neem and Rice Bran oils are locally available and they give encouraging results when used in diesel engines [16-25]. These non edible oils could be regarded as alternative fuels for CI engine applications. Table 1 compares some of the important properties of different non-edible vegetable oils, which are used as fuels in diesel engines.

A number of vegetable oils have been tested all over the world to evaluate their performance in diesel engines. Some of them like neem oil, palm oil, Honge oil, rape seed oil, coconut oil, cottonseed oil, Jatropha oil, Mahua, Rice Bran and Rubber seed oils have been found to be viable.

Studies have revealed that some of these oils can directly substitute diesel in electricity generating sets and irrigation pump sets with no modifications. Such oils when used are commonly known as 'Straight Vegetable Oils' (SVO). Several non edible oils are considered for the present work.. The following oils are only explained as they are available in plenty locally and are considered for this present study.

Table 1. Properties of non edible vegetable oils*

Properties	Diesel	Honge oil	Jatropha oil	Rape seed oil	Cotton seed oil	Rubber seed oil	Tobacco seed oil
Density (kg/m^3)	840	927	918	918	874	926	920
Calorific Value (kJ/kg)	42390	35800	39774	36890	39648	38957	39400
Cetane Number	45-55	40	45	39	45	40	38
Viscosity (cst) @ 40 ^{0}C	4.59	56	49.9	55	50	55.6	27.7
Flash point (^{0}C)	75	250	240	275	210	242	220
Carbon Residue (%)	0.1	0.66	0.44	0.31	0.55	0.46	0.57

* Source: Yusufumi Takeda, 1983; Heywood, 1988; Culshaw, 1993; Gopalkrishnan *et al.,* 1992; Gubitz *et al.,* 1999; Nwafor *et al.,* 2000; Amba Prasad Rao and Ram Mohan, 2002; Ayhan Demirbas, 2002; Giannelos *et al.,* 2002; Raheman and Phadatare, 2004; Ramadhas *et al.,* 2005; Barnwal *et al.,* 2005.

Honge, Rice Bran and Neem Oils

Honge tree is chiefly found along the banks of streams and rivers or near the seacoast. The Honge oil is popularly known as *Pongamia Pinnata* or Karanja oil. The Honge oil is extracted from the seeds of Honge tree also called Karanja tree. Rice Bran oil is a high viscosity, low volatility and polyunsaturated character of non edible oil. The crude Rice Bran oil (CRBO) is obtained from the outer brown layer of rice. India is the largest producer of rice in the world next to China, having a potential to produce about 10 lack tons of Rice Bran oil per annum. Rice Bran oil (CRBO) is non-toxic and biodegradable and is adequately available at reasonable price. Rice Bran oil is unique in terms of high thermal and oxidation stability and therefore reasonably free from rancidity. Presence of multi-component system of natural anti-oxidants prevents Rice Bran oil from getting rancid. Neem oil is acried, yellow, bitter in taste and has disagreeable garlic like odors. It is best used in pharmaceutical and pesticides industry. It is used as antifeedant, repellant, insecticide and growth disruptor. Refined neem oil is used for manufacture of technical oleic acid, stearic acid and production of quality soaps. It is used to treat skin diseases like scrofula indolent, ulcer, sores and ringworms. Present demand for the production of herbal medicine and herbal-based cosmetics is around 30% to35 %. The neem oil consists of Linoleic Acid - 2.1%, Various Lower Fatty Acids - 2.3%, Palmitic Acid - 12.6% , Stearic Acid - 21.4% and Oleic Acid - 52.8% .

Neat use of vegetable oils poses some problems when subjected to prolonged usage in CI engines. Vegetable oil has higher viscosity and lower volatility and causes improper atomization of fuel during injection. This leads to smoky exhaust in a diesel engine. The other problems are clogging of nozzle orifice, poor atomization and vaporization and results in incomplete combustion. The higher viscosity of oil changes the spray pattern and droplet size. The longer engine trials have resulted in injector chocking, engine deposits, ring sticking, thickening of engine and lubricating oil which reduces engine life. Also wax depositions on the filter element with engine operation on such oils are common. The polyunsaturated nature of the vegetable oil causes long-term problems due to slow polymer gum formation causing ring sticking. Because of these problems, vegetable oils need to be converted into more compatible fuels for existing engines. The fuel modification is mainly aimed at reducing the viscosity and increasing volatility. The different methods are preheating, blending, transesterification, super critical methanolysis and ultrasonic assisted transesterification. More recently, for continuous biodiesel production microwave assisted continous transesterification process is also reported in the literature.

Transesterification is a method to reduce the viscosity of vegetable oils to produce esters (commonly known as Biodiesel) of respective oils. In transesterification process a triglyceride reacts with three molecules of alcohol in the presence of a catalyst, producing a mixture of fatty acids alkyl esters and glycerol [8, 9, 12, 19]. Conversion of vegetable oil to biodiesel is affected by different parameters namely time of reaction, reactant ratio (Molar ratio of alcohol to vegetable oil), type of catalyst, amount of catalyst, temperature of reaction, rate of stirring [8,9]. The molecular weight of a typical ester molecule is roughly one third that of typical oil molecule and therefore has a very low viscosity. To complete a transesterification process stoichiometrically, 3:1 molar ratio of alcohol to triglycerides is needed. However in practice higher ratio of alcohol to oil ratio is generally employed to obtain biodiesel of low viscosity and high conversion. In the present study these factors affecting the transesterification process

of Hong, Rice Bran and Neem oils have been studied and optimum parameters are determined the biodiesel yield.

Biomass Gasification Status in India

India being predominantly agricultural country requires major attention for the fulfillment of energy demands of a farmer. In India nearly 24,500 villages are classified as remote villages and these villages needs electric supply from renewable energy based decentralized electricity generating options such as biomass gasifiers, PV and wind energy conversion systems under a program initiated by ministry of non-conventional energy sources of Government of India. The focus is mainly on deployments of biomass gasifier power project. Also the biomass resources for power generation are distributed throughout the country for decentralized power supply in India. Through gasification technology, waste agro materials can be converted into a fuel source for running internal combustion engines. Producer gas generated from the gasification of solid carbonaceous fuel such as wood, charcoal, coal or coke, agricultural wastes and agro-industrial wastes in a gasifier has a good potential as an alternative fuel. The technology of gasification is reasonably well established in India and the efficiency of conversion of biomass to producer gas is quite high (75-80%). With an octane rating of 100 to 105, calorific value of 5 to 6 MJ/Nm^3, and lower engine emissions, producer gas as an alternative fuel for diesel engine on dual fuel mode of operation has a bright future in a biomass rich country like India. In view of this, promotion of biomass-based power generation in the country is being encouraged. Producer gas obtained from downdraft gasifier can act as a promising alternative fuel, especially for diesel engines by substituting considerable amount of diesel oil. Dual fuel compression ignition engines utilizing a combination of liquid fuels as injected fuels and CNG, LPG, Hydrogen and producer gas as inducted fuels have been investigated by many researchers [26-33]. However dual fuel compression ignition engines utilizing a combination of non edible oils as injected fuels and producer gas as inducted fuel have been investigated by few researchers [49, 50]. This can pave the way for sustainable energy growth by providing energy security for our country. Suitable utilization of gaseous fuel resources with liquid non edible oils can minimize exhaust emissions without excessive increase in cost compared to conventional diesel engines operating on fossil fuels. Several researchers have undertaken works related to conservation of diesel fuel in dual fuel engines using various vegetable oils [34-56]. Dual fuel combinations of Producer gas-Honge oil, Producer gas-Rice Bran oil and Producer gas-Neem oil have been extensively studied for rural applications [57]. This feature is very convenient for electricity generation in more remote areas or areas inaccessible for long periods over the year. The major problem with producer gas operated gas engines is power derating. From the fuel flexibility point of view, dual fuel engines are highly acceptable. Modification of existing diesel engine for dual fuel operation with producer gas is simple.

The present work is undertaken to investigate feasibility of popular alternative fuels in the form of non edible oils of Honge, Rice bran and Neem oils and their esters in single fuel mode and combinations of these oils with producer gas in dual fuel mode. Experiments were conducted to optimize parameters in terms of injection timings and injection pressures for each fuel combinations selected. Honge oil gave better overall performance associated with reduced emissions in both single and dual fuel mode. Dual fuel mode of operation for all the

fuel combinations resulted in poor performance at all the loads and injection timings compared to single fuel operation. However dual fuel operation with all the fuel combinations resulted in lower smoke, NOx and increased CO emissions.

2. FUELS USED AND THEIR PROPERTIES

The properties of the Crude and methyl ester derived from Honge, Rice bran and Neem oils have been determined and summarized in Table 2 and 3.

Table 2. Properties of Diesel, Honge, Rice Bran and Neem oils [8]

Sl No	Properties	Diesel	Honge oil	Rice Bran Oil	Neem oil	ASTM Test Number
1	Density Kg / m^3	840	918	922	927	D4052
2	Sp gravity	0.840	0.918	0.922	0.927	--
3	KV (cSt) @ 40 ^{0}C	3.5	44.850	46.815	20.50	D445
4	Flash point (^{0}C)	56	270	285	34	D93
5	Calorific value (kJ/kg)	43,000	35800	43135	39,501	D240

Table 3. Properties of Diesel, HOME, ROME and NOME [8]

Sl No	Property	Diesel	HOME	ROME	NOME	ASTM Test Number
1	Density (kg/m^3)	840	870	877	880	D4052
2	Sp. gravity	0.840	0.870	0.870	0.882	--
3	K V (cSt) @ 40^0 C	3.5	5.5	5.29	5.24	D445
4	Flash point (^{0}C)	56	170	183	170	D93
5	Calorific value (kJ/kg)	43,000	36,100	42200	39500	D240

3. EXPERIMENTAL SETUP

Figure 1 shows the schematic diagram of the experimental set up used for the study. The specifications of the engine and the down draft gasifier are shown in table 4 and 5 respectively. An eddy current dynamometer is used for loading the engine. The fuel flow rate is measured on the volumetric basis using a burette and stop watch. The engine and dynamometer were interfaced to a control panel, which is connected to a digital computer. The exhaust gases HC, CO, CO_2, NO_X were determined by a five gas analyzer of Delta 1600s series make. The specifications of the five gas analyzer are given in Table 7. A DELTA 1600 S Exhaust Gas Analyzer based on a Non-Dispersive Infrared technology (NDIR) was used for measuring exhaust emissions. Exhaust emissions of unburned hydrocarbons (CO, HC as n-Hexane equivalent: C_6H_{14}, CO_2) is measured by directing an infrared light through the sample cell to the optical block. Hydrocarbons were measured in parts per million (ppm) hexane

equivalent and carbon monoxide emissions were measured in terms of percentage volume. Oxygen and NO_X gas concentrations are measured by using electrochemical (fuel cell) sensors.

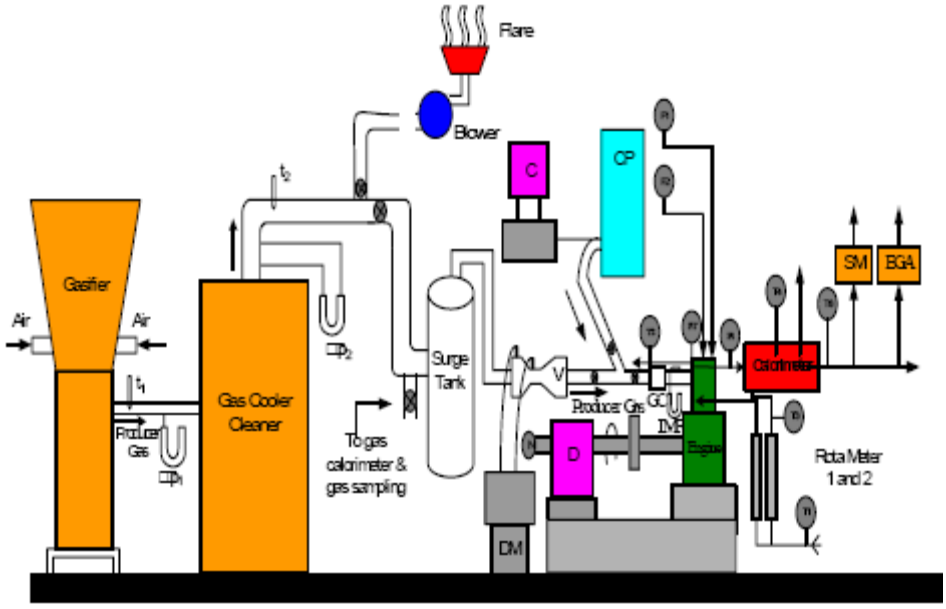

Figure 1. Schematic diagram of the Experimental set up.

Table 4. Specifications of the engine

Make and Model	Kirloskar, TV1
No. of Cylinders	One
Orientation	Vertical
Cycle	4 Stroke
Ignition System	Compression Ignition
Bore X Stroke	87.5mm X 110mm
Displacement Volume	660 cc
Compression Ration	17.5 : 1
Arrangement of valves	Overhead
Combustion Chamber	Open Chamber (Direct Injection)
Rated Power	5.2 kW (7 HP) @1500 rpm
Cooling Medium	Water cooled

The smoke opacity is measured by using Hartridge smoke meter. The specifications of the smoke meter are given in Table 6. Exhaust smoke density was measured with the help of Hartridge Smoke meter. The smoke meter works on the principle of comparative basis. It contains two dimensionally and optically similar tubes. The reference tube is connected to the clean air blower. Air is drawn from the clean air inlet through a damper. The smoke tube is connected to the smoke inlet via the smoke bypass valve. This inlet track contains a temperature sensor, moisture trap and has a pressure relief valve controlled outlet, a pick off for the manometer connection and a vane at the tube entry.

Table 5. Specifications of the down draft gasifier

Type	Downdraft gasifier
Supplier	Ankur Scientific Energy Technologies Pvt. Ltd., Baroda.
Rated capacity	62735 kJ/h
Rated Gas flow	15 Nm^3/h
Average gas calorific value	5-5.6 MJ/m^3
Rated woody biomass consumption	5-6 kg/h
Hopper storage capacity	40 kg
Biomass size	10 mm (Minimum) 50 mm (Maximum)
Moisture content (DB)	5 to 20%
Typical conversion efficiency	70-75%
Typical gas composition	CO=19$\pm$3%, CO_2=10$\pm$3%,N_2=50%, H_2=18$\pm$2%,CH_4= upto3%

Table 6. Specifications of smoke meter

Type	HARTRIDGE SMOKEMETER-4
Object of Measurement	Smoke
Measuring range opacity	0 – 100 %
Accuracy	+ / -2 % relative
Resolution	0.1 %
Smoke length	0.43 m
Ambient Temperature Range	-5^0 C to + 45^0 C
Warm up time	10 min. (self controlled) at 20^0C
Speed of Response Time	Within 15 sec. for 90% response
Sampling	Directly sampled from tail pipe
Power Supply	100 to 240 V AC / 50HZ 10 – 16 V DC @15 amps
Size	100 mm x 210 mm x 50 mm.

Table 7. Specifications of exhaust gas analyzer

Type	DELTA 1600S
Object of Measurement	Carbon monoxide (CO), Carbon Dioxide (CO_2) and Hydrocarbons (HC)
Range of Measurement	HC = 0 to 20,000 ppm as C_3H_8 (Propane) CO = 0 to 10% CO_2 = 0 to 16% O_2 = 0 to 21% NO_X = 0 to 5000 ppm (as Nitric Oxide)
Accuracy	HC = +/- 30 ppm HC CO = +/- 0.2% CO CO_2 = +/- 1% CO_2 O_2 = +/- 0.2% O_2 NO_X = +/- 10 ppm NO
Resolution	HC = 1 ppm CO = 0.01% Vol. CO_2 = 0.1% Vol. O_2 = 0.01% Vol. NO_X = 1 ppm
Warm up time	10 min. (self controlled) at 20^0C
Speed of Response Time	Within 15 sec. for 90% response
Sampling	Directly sampled from tail pipe
Power Source	100 to 240 V AC / 50Hz
Weight	800 g
Size	100 mm x 210 mm x 50 mm

The light source and photoelectric cell are each mounted on an arm pivoted on each end of a spring located control shaft, which is operated by a control knob. The opacity of the smoke sample was compared to a clean air sample by first taking reading through the clean air tube to set the zero, then moving the light and photoelectric cell to the smoke tube for an instantaneous comparative reading of the opacity of the tube sample.

The engine tests were conducted on four stroke single-cylinder direct injection water-cooled CI engine. The engine was always operated at a speed of 1500 rev/min. The engine had a conventional fuel injection system. The injection nozzle had three holes of 0.3mm diameter with a spray angle of 120◦. The injector opening pressure (IOP) and the static injection timing as specified by the engine manufacturer were 205 bar and 23^0 before top dead centre (BTDC), respectively. The engine had been provided with a hemispherical combustion chamber with overhead valves operated through push rods. Cooling of the engine was accomplished by circulating water through the jackets of the engine block and cylinder head. Experiments were conducted under a thermal steady-state condition of the engine with an inlet cooling water temperature of 50^0C. A piezoelectric pressure transducer was mounted flush with the cylinder head surface to measure the cylinder pressure. The engine was started on neat diesel fuel and the readings were recorded at steady state conditions. Similar procedures were repeated for the Honge Oil Methyl Ester (HOME), Rice Bran Oil Methyl Ester (ROME) and Neem Oil Methyl Ester (NOME) in single fuel mode and with producer gas in dual fuel combination.

Experimental Heat Release Estimation

The heat release rate of the fuel causes a variation of gas pressure and temperature within the engine cylinder. It strongly affects fuel economy, power output, and the emissions of the engine [58-69]. In-cylinder pressure and top dead centre signals were acquired and stored on a high-speed computer-based digital data acquisition system. The data from 100 consecutive cycles were recorded. The heat release rate was calculated by using the first law analysis of the pressure crank angle data. Net heat release rates were calculated using single zone Heat Release Model [62].

4. RESULTS AND DISCUSSION

4.1. Single Fuel Operation

4.1.1. Crude Honge, Rice Bran and Neem Oil Operation

In single fuel mode of operation, non edible vegetable oils of Honge, Rice bran and Neem oils were considered for the study. The long term operation of the engine with crude oils of Honge, Rice bran and Neem resulted in poor performance with the following problems as shown in Figure 2 to 7.

- Carbon deposits on cylinder head and piston top surface (Figure 2)
- ring sticking (figure 3)

- Carbon deposits on cylinder head (figure 4)
- wax depositions on the filter element (figure 5)
- carbon deposits on injector tips (figures 6 and 7)

Figure 2. Carbon deposited Piston top surface.

Figure 3. Ring sticking with crude oil engine operation.

Figure 4. Carbon deposits on cylinder head with crude oil engine operation.

Figure 5. Wax depositions on the filter element with crude oil engine operation.

Figure 6. Injector tip of diesel fuelled engine.

Figure 7. Injector tip of crude oil fuelled engine.

4.1.2. Biodiesel Operation

Biodiesel is a fatty acid alkyl ester, which can be derived from any vegetable oil by transesterification. In this study, Honge, Neem and Rice bran oils were transesterified with methanol using sodium hydroxide as catalyst to obtain their respective biodiesel. These biodiesel were named Honge oil methyl ester (HOME), Neem oil methyl ester (NOME) and Rice bran oil methyl ester (ROME) respectively. These biodiesel were than tested in a single cylinder, four stroke, direct injection, and compression ignition diesel engine to evaluate the performance, emission and combustion characteristics. All the tests were conducted at different loads and for three injection timings of 23^{o} BTDC and injection pressure of 205 bar.

Performance Characteristics

The effect of brake power on brake thermal efficiency for Diesel, HOME, ROME and NOME is shown in Figure 8. For all the injected ester fuels a steady increase in efficiency with load was observed. All the esters of vegetable oils tested showed lower brake thermal efficiency compared diesel. The poor mixture formation tendency of ester fuels associated with their low volatility, higher viscosity and density are the reasons for this observed trend. Among the biodiesels tested the maximum brake thermal efficiency was recorded with HOME and is 30.4 % at 80 % power output compared to 31.25 % for diesel. However, the brake thermal efficiencies values for ROME and NOME were 29.50, and 28.00 % respectively at 80% load.

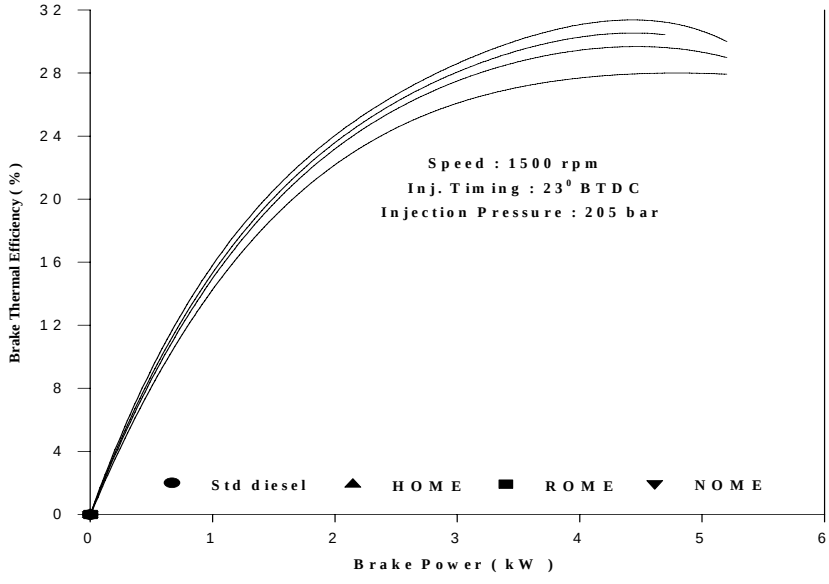

Figure 8. Effect of Brake Power on Brake Thermal Efficiency.

Emission Characteristics

Figure 9 shows the effect of brake power on smoke opacity for Diesel, HOME, ROME and NOME. The heavier molecular structure of the ester fuels due to higher viscosity, results

in poor atomization and this leads to higher smoke emission. At 80% load smoke opacity values were 66, 69 and 62 HSU for ROME, NOME and HOME respectively compared to 53 HSU with diesel operation.

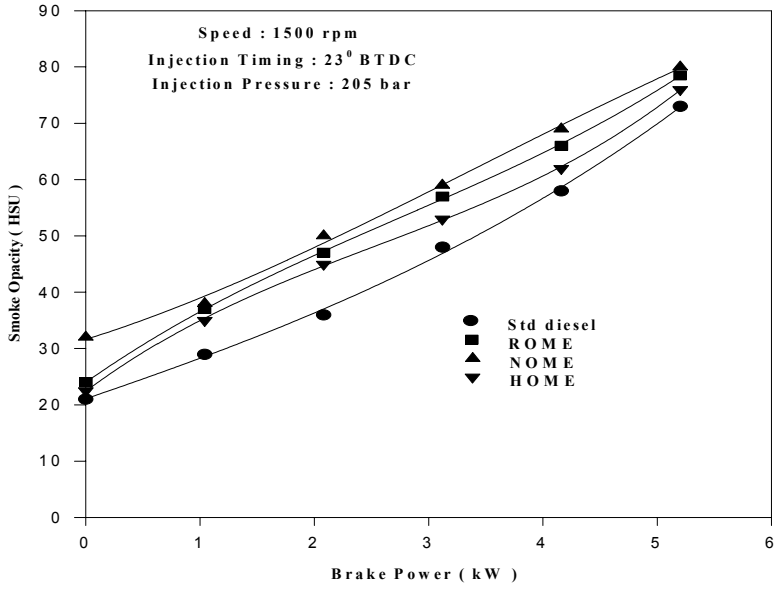

Figure 9. Effect of Brake Power on Smoke Opacity.

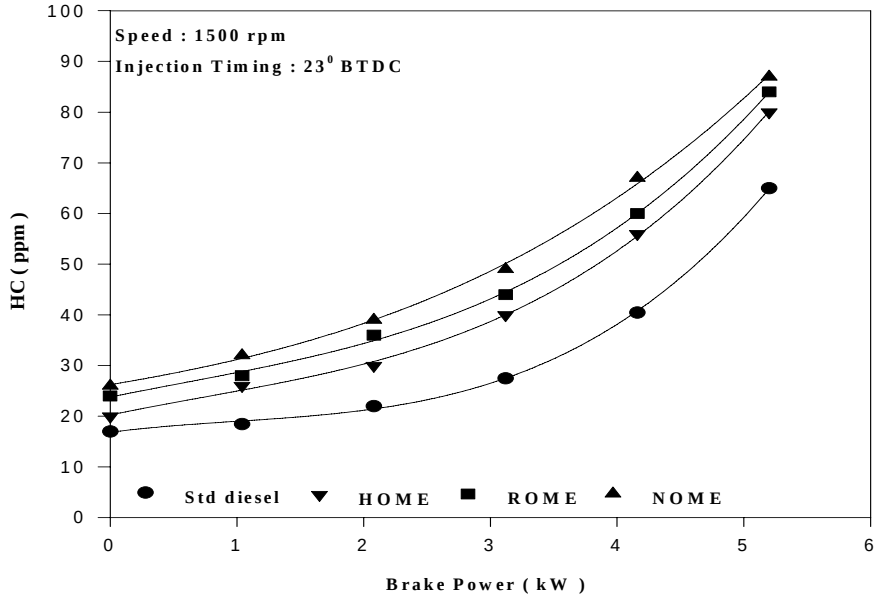

Figure 10 Effect of Brake Power on HC Emission.

The effect of brake power on HC and CO emissions for all the injected fuels are shown in shown in Figures 10 and 11 respectively. Hydrocarbon emissions with biodiesels were higher compared to standard diesel oil. The lower brake thermal efficiency and improper mixing of

fuel and air due to relatively poor atomization with lower volatility of biodiesel oil is responsible for this trend.

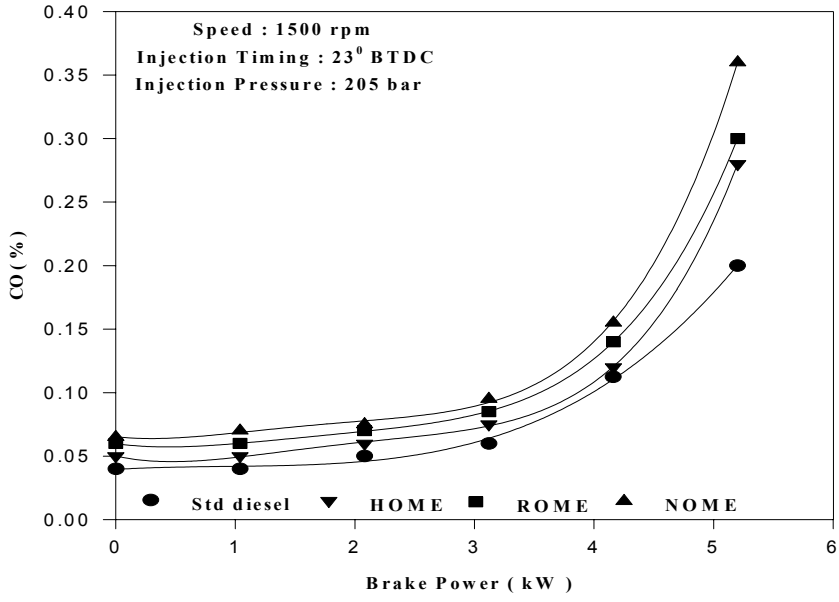

Figure 11. Effect of Brake Power on CO Emission.

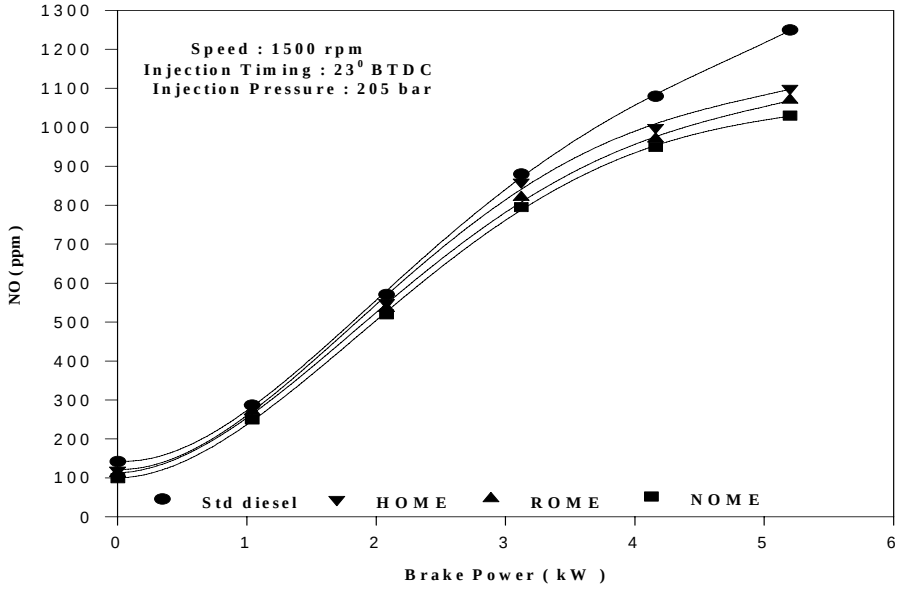

Figure 12. Effect of Brake Power on NO Emission.

Among the biodiesels tested HC emission values were 67, 56 and 60 ppm for NOME, HOME and ROME respectively compared to 40.5 ppm with diesel operation at 80% load.

Similar trend is observed for carbon monoxide as well in the exhaust as that of HC emission. Carbon monoxide values were 0.155, 0.12 and 0.140% for NOME, HOME and HOME respectively compared to 0.1125% with diesel operation at 80% load.

The effect of brake power on nitrogen oxide emissions is shown in Figure 12. It was observed that NO_X emissions were higher for diesel operation compared to biodiesel. Heat release rates of biodiesels were lower during premixed combustion phase, which will lead to lower peak temperatures. Nitrogen oxides formation strongly depends on peak temperature, which explains the observed phenomenon. Nitrogen oxides emission values were 950, 1000 and 970 ppm for NOME, HOME and ROME respectively compared to 1080 ppm with diesel operation at 80% load.

4.2. Dual Fuel Operation of Vegetable Oils with Producer Gas

Gasifiers are the reactors in which gasification of solid fuel takes place giving Producer gas. This gasification is carried out in different types of gasifiers. These are downdraft, updraft and cross draft, fluidized, entrained bed, rotary and inclined grate. The most common gasifier is the downdraft or co-current type. Figure 13 shows schematic view of a downdraft gasifier. The pyrolysis zone is above the combustion zone and the reduction zone below it. Fuel is fed from the top and the air flows in the downward direction through the combustion and reduction zones. Movement of air is in the same direction as that of the fuel. The down draft gasifier is so designed that tars in the pyrolysis zone are drawn through the combustion zone wherein a high amount of them will be cracked and reduced to non-condensable gaseous products before leaving the gasifier. The internal diameter in most downdraft gasifiers is reduced in order to create throat. Air inlet nozzles are commonly set radially round the throat to distribute air as uniformly as possible.

The Producer gas leaving a gasifier has a fairly high temperature (300-400 ^oC for wood gas and 400-500 ^oC for charcoal gas). It is mixed with solids (soot and ashes) and steam vapour as well as traces of tar, which will cause wear of the engine components. This in turn could cause serious problems if not removed before the gas enters the engine. It is therefore essential that the gas is sufficiently cooled and cleaned. Cooling increases the volumetric efficiency of the gas and assists in cleaning of the gas. Cleaning of gas is essential otherwise impurities will cause problems like excessive wear, carbon deposits, pitting of the valve seats, sticky valves and rings, deteriorating of lubricating oil, slow starting and heat build-up in the engine. Producer gas for internal combustion engine applications requires impurities to be removed to acceptable levels (dust < 50 mg/m^3, tar < 50 mg/m^3 and acids < 50 mg/m^3). Cleaning equipment consists of cyclones, fabric filters, scrubbers and electrostatic precipitators. A down draft gasifier-engine system as shown in Figure 14 is built as a unit and fine-tuned for a successful operation. A gasifier-engine system consists of a gasifier, a gas cooling and cooling train and a compression ignition engine on dual fuel operation. The gasifier is connected to suction side of engine through cooler cleaner unit. Engine draws in a mixture of air and Producer gas.

This mixture is compressed and ignited by a pilot diesel spray. The combustion is initiated by large number of diesel droplets but later progresses as turbulent flame propagation in lean premixed mixture of air and gaseous fuel. Since both fuels are

simultaneously used, this mode of operation is called dual-fuel. The amount of pilot quantity required in case of Producer gas is 10-20% of full load diesel consumption.

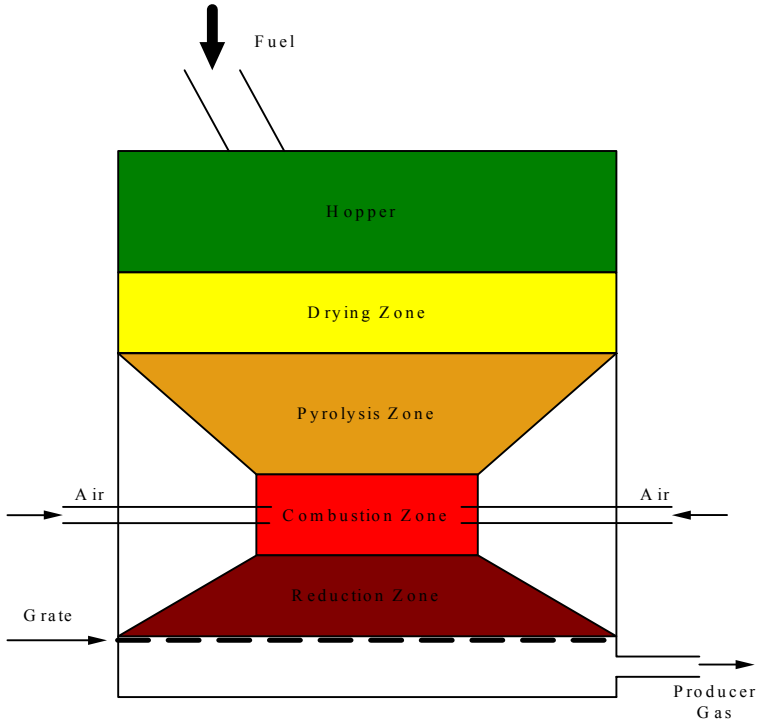

Figure 13. Schematic Diagram of a Downdraft Gasifier.

Figure 14. A down draft gasifier-engine system.

Figure 15. Gasifier Operation.

Figure 16. Wood burning as viewed through tuyer.

The maximum diesel substitution by Producer gas in a dual fuel operation is about 80 percent. Figure 15 shows gasifier operation. Figure 16 shows wood burning as viewed through tuyuer. Figure 17 shows flaring of the Burner for checking gas quality. Figure 18 shows the view of the fabric filters used for cleaning Producer gas before and after the dual fuel engine operation.

Figure 17. Flaring of the Burner for checking gas quality.

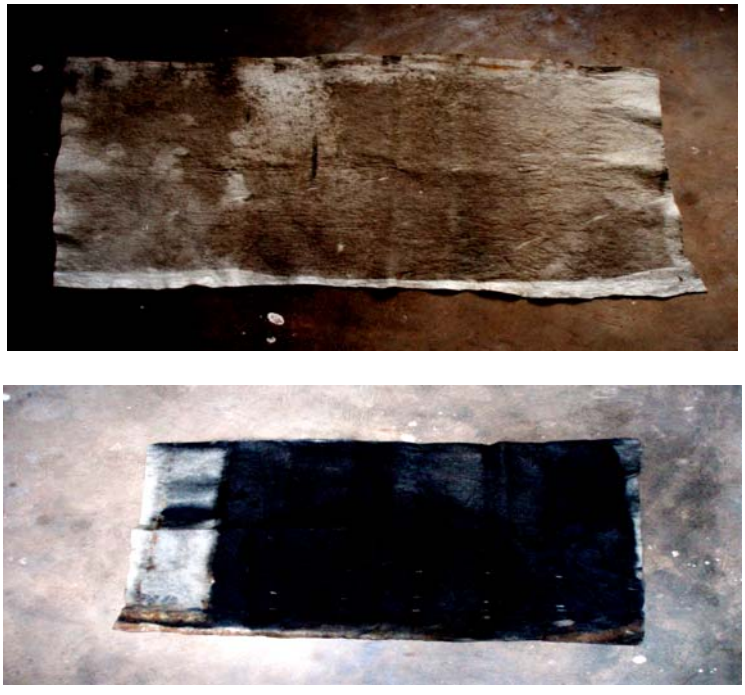

Figure 18. Fabric filters used for cleaning Producer gas before and after dual-fuel operation fuelled with diesel and biodiesel.

The performance evaluation of CI engine is carried out to compare dual fuel mode of operation. The magnitude of engine de-rating is in the order of 29% and this depends mainly on the parameters like injection pressure and timing. Vegetable oil would be conveniently used as a diesel substitute in diesel engine.

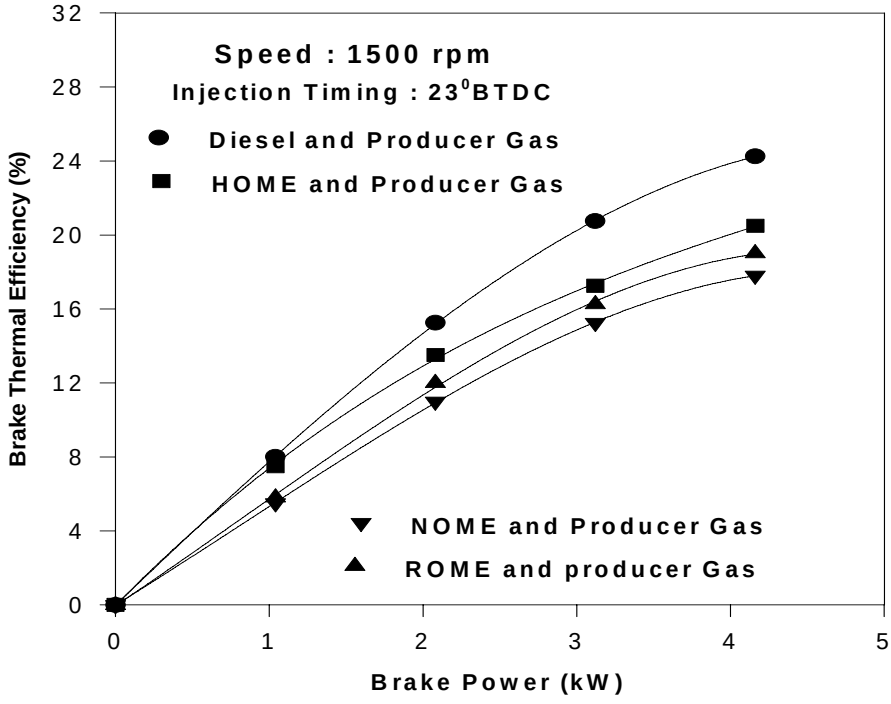

Figure 19. Effect of Brake Power on Brake Thermal Efficiency for dual fuel operation.

The marginal decrease in brake thermal efficiency, marginal increase in brake fuel consumption, and decrease in brake power, torque and comparable emissions make the Honge, rice Bran and Neem oils suitable alternative fuels for diesel engine. The brake thermal efficiency (Figure 19) is found to be higher for producer gas-diesel dual fuel mode of operation compared to HOME- Producer gas and NOME-Producer gas and ROME-Producer gas operation over the entire load range. Producer gas being common, properties of the injected fuel has a major effect on the engine performance. All the injected fuels have higher viscosity than diesel which makes atomization difficult and also has lower calorific value, which together result in lower brake thermal efficiency. The brake thermal efficiency values were 24.2500, 20.5000% 19.0000% and 17.8000 at 80% with Producer gas-diesel, Producer gas-HOME, Producer gas-NOME and Producer gas-ROME respectively. The smoke opacity was lower for Producer gas-diesel dual fuel operations compared to HOME- Producer gas and NOME-Producer gas and ROME-Producer gas operation over the entire load range (Figure 20).

The heavier molecular structure of all the injected fuels compared to diesel results in higher smoke levels. The smoke opacity of 34.5 HSU, 57.5 HSU, 61.0000and 65.0000HSU were obtained with Producer gas-diesel, Producer gas-HOME, Producer gas- NOME and Producer gas- ROME respectively.

Figures 21 and 22 shows the effect of brake power on HC and CO emissions respectively. Hydrocarbon emissions were higher throughout the load range for the injected vegetable oils compared to Producer gas-diesel. The exhaust emissions of carbon monoxide were lower for Producer gas-diesel dual fuel operations compared to Producer gas-HOME, Producer gas-

NOME and Producer gas-ROME respectively. This may be due to higher heat release during premixed burning phase rather than diffusion burning phase with Producer gas-diesel mixture.

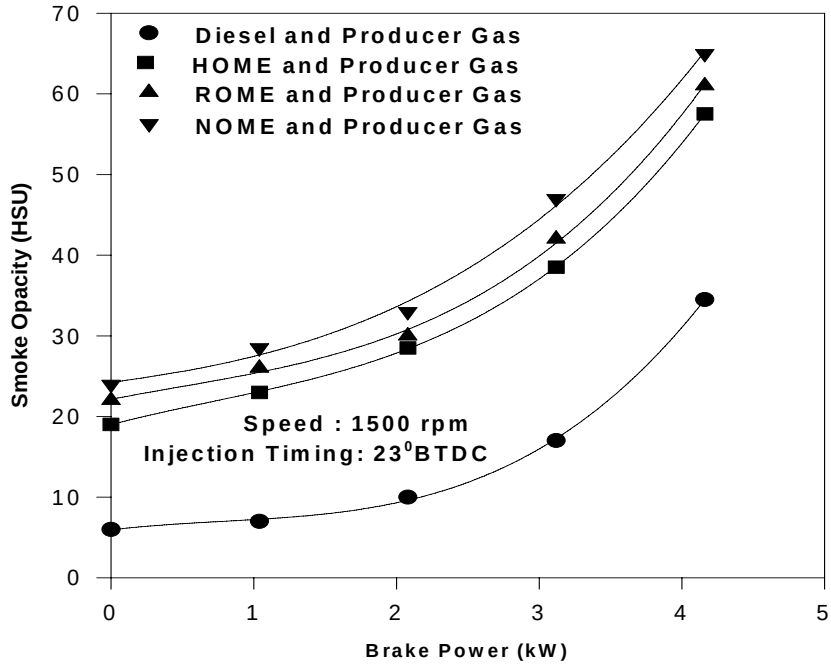

Figure 20. Effect of Brake Power on smoke opacity for dual fuel operation.

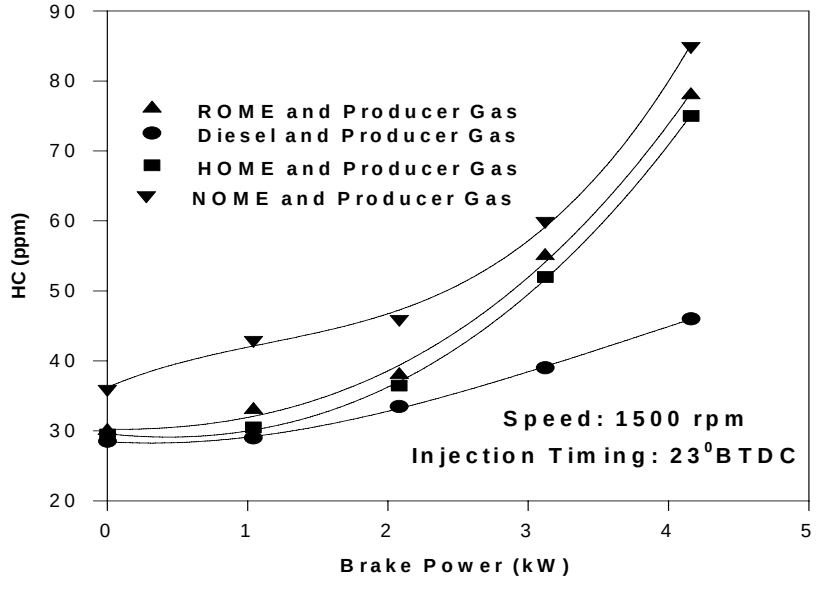

Figure 21. Effect of Brake Power on of HC for dual fuel operation.

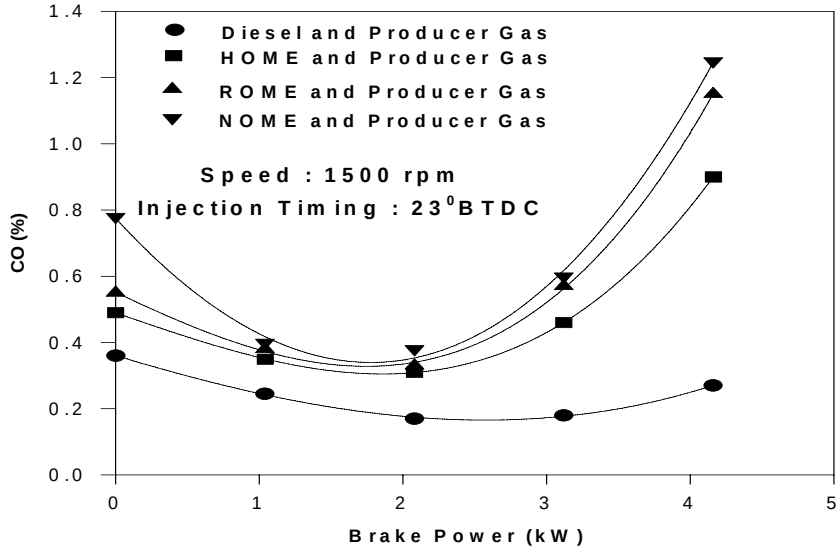

Figure 22. Effect of Brake Power on CO for dual fuel operation.

Nitrogen oxides emissions in dual fuel mode (Figure 23) do not vary significantly with the change in injected fuel. NOx emissions were lower for Producer gas –diesel dual fuel operation. Nitrogen oxide emissions in dual fuel mode of operation were 130 ppm, 195 ppm 200 and 212 ppm with diesel, HOME, NOME and ROME as injected fuel respectively. Higher NOx emissions for injected esters of vegetable oils in dual fuel operation may be due to availability of higher oxygen that is present in the injected esters of vegetable oils molecular structure. Also for the same power output more esterified oils are required (due to increased specific fuel consumption) leading to delayed injection.

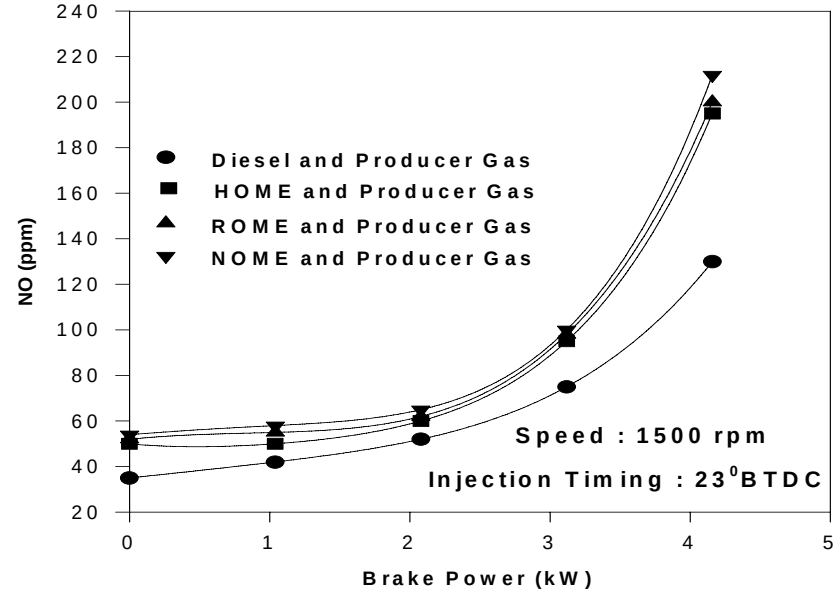

Figure 23. Effect of Brake Power on NO for dual fuel operation.

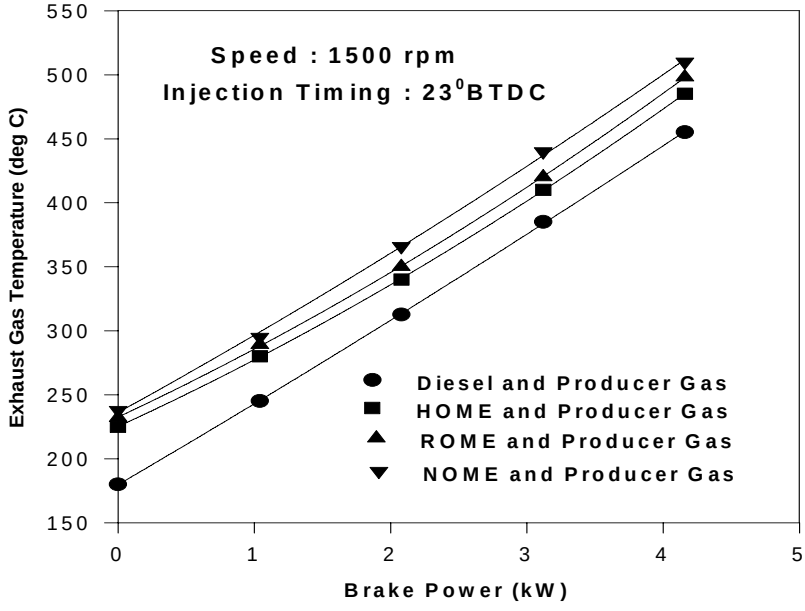

Figure 24. Effect of Brake Power on Exhaust Gas Temperature for dual fuel operation.

Exhaust gas temperature at different power outputs in dual fuel mode of operation is presented in Figure 24. The EGT is found to be higher for Producer gas-ester oils and lower for Producer gas-Diesel operation. The exhaust gas temperature of 455, 485, 498 and 510^{0}C were observed with Producer gas-diesel, Producer gas-HOME, Producer gas-NOME and Producer gas-ROME respectively.

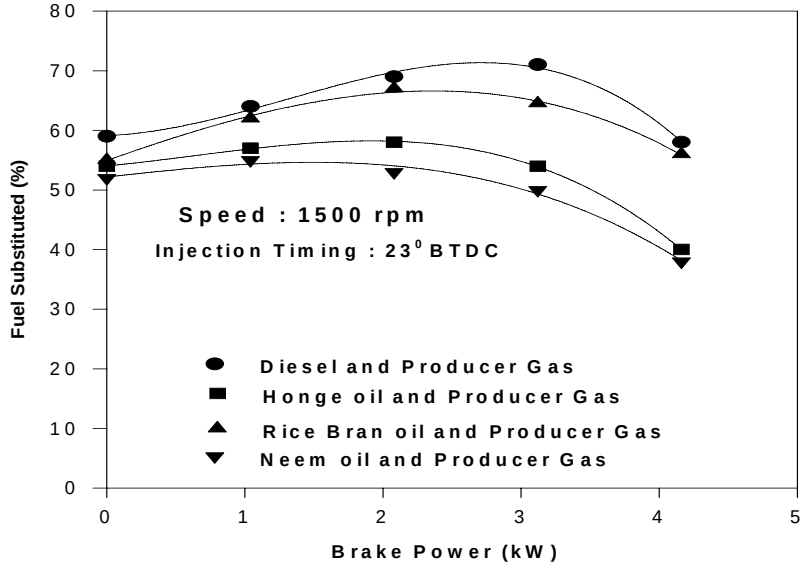

Figure 25. Effect of Brake Power on fuel substituted for dual fuel operation.

Figure 25 presents the fuel substitution for dual fuel operation at different power outputs. Fuel substitution values were maximum for diesel- Producer gas operation compared to

vegetable oil combinations. Injected fuel properties such as cetane number, viscosity and calorific value may be considered as responsible for the observed trend. The percentage of respective fuels substituted with Producer gas-diesel, Producer gas-Honge oil, Producer gas-Rice Bran oil and Producer gas-Neem oil respectively were 71.00%, 54.00%, 64.50% and 50.

4.3. Overall Comparison of the Different Modes of Engine Operation

This section compares the optimum results obtained with different modes of operation in which Honge oil was used as the main fuel in a CI engine. The comparison has been made at 80 % power output. The engine has been operated on single fuel mode and dual fuel mode with following fuel combinations.

a) Neat Honge, Rice Bran and Neem oils.
b) Esters of Honge oil, Rice Bran oil and Neem oils.
c) Dual fuel operation with Honge, Rice Bran and Neem oil methyl esters as the injected fuels and producer gas as the inducted fuel.

Figure 26 shows variation of brake thermal efficiency with different modes of engine operation. Highest brake thermal efficiency is obtained with all the esters tested in single fuel operation. Dual fuelling the engine with esters along with producer gas results in lower thermal efficiency.

The exhaust gas temperature shown in Figure 27 is relatively similar with both the modes of operation. However dual fuel operation in general resulted in slightly higher exhaust gas temperatures compared to single fuel mode.

Figure 28 shows smoke levels with different modes of engine operation. It is observed that smoke emissions are higher for esters in single fuel mode of operation. As an overall comparison it is observed that the dual fuel operation resulted in lower smoke emissions.

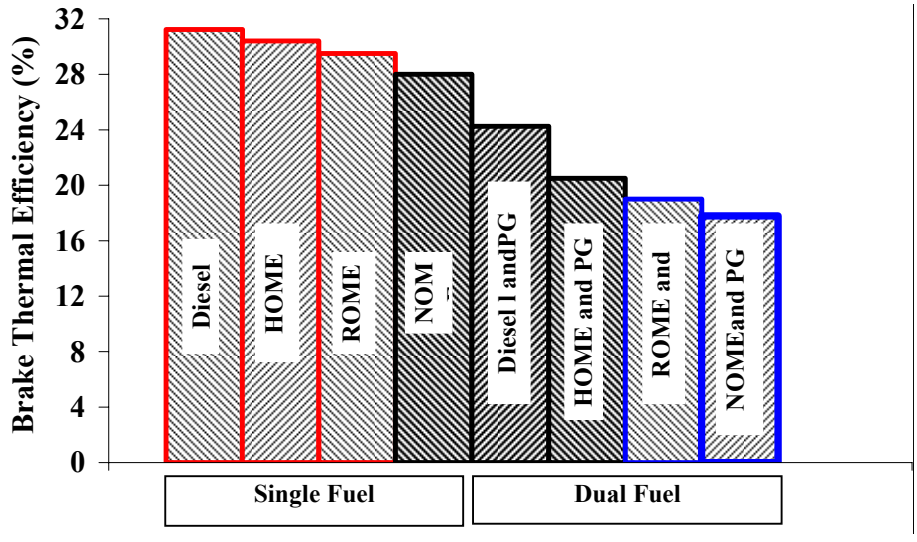

Figure 26. Variation of Brake Thermal Efficiency with Different Modes of Engine Operation.

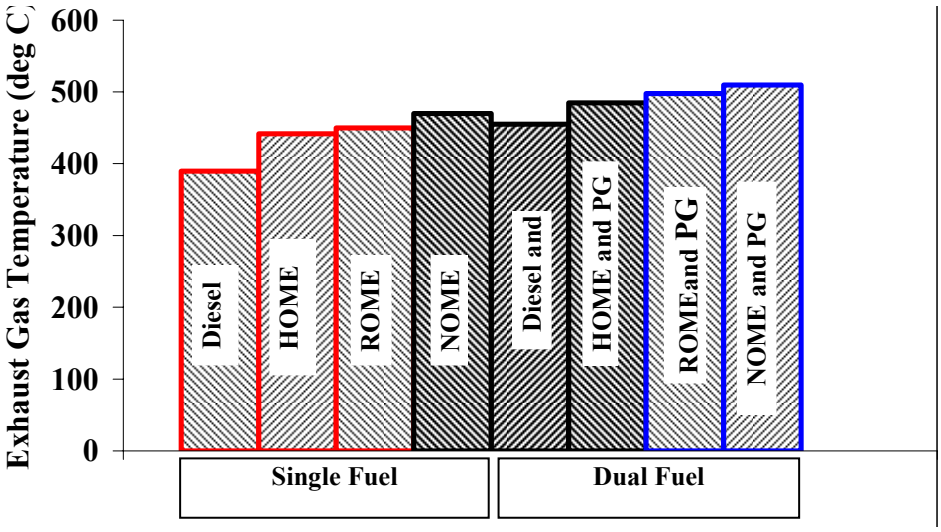

Figure 27. Variation of Exhaust gas Temperature with Different Modes of Engine Operation.

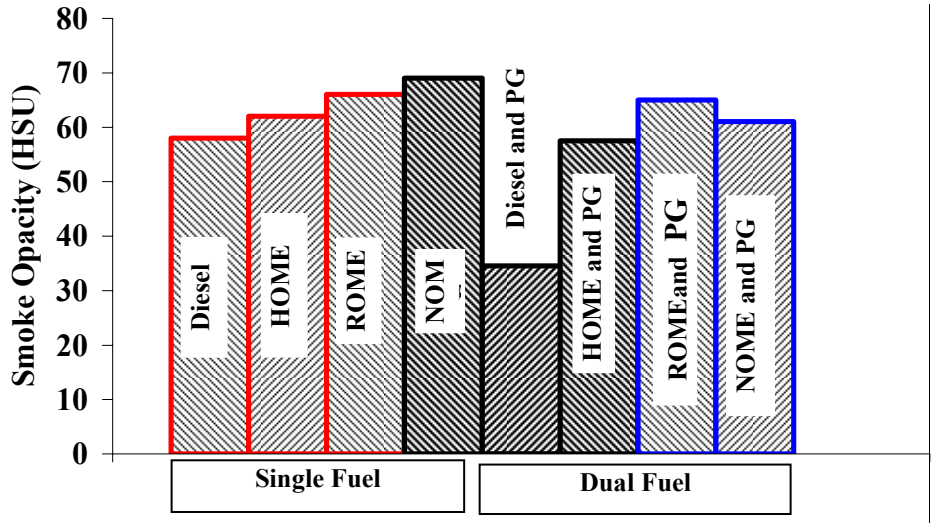

Figure 28. Variation of Smoke Opacity with Different Modes of Engine Operation.

Figure 29 show hydrocarbon at 80% power output with different modes of engine operation. It is seen that in single fuel operation with esters lower hydrocarbon were observed than dual fuel operation.

Figure 30 show carbon monoxide emissions at 80% power output with different modes of engine operation. It is seen that in single fuel operation with esters lower carbon monoxide emissions were observed than dual fuel operation.

Figure 31 shows NO variation with different modes of engine operation. Dual fuel operation recorded lower NO_X emissions compared to single fuel operation.

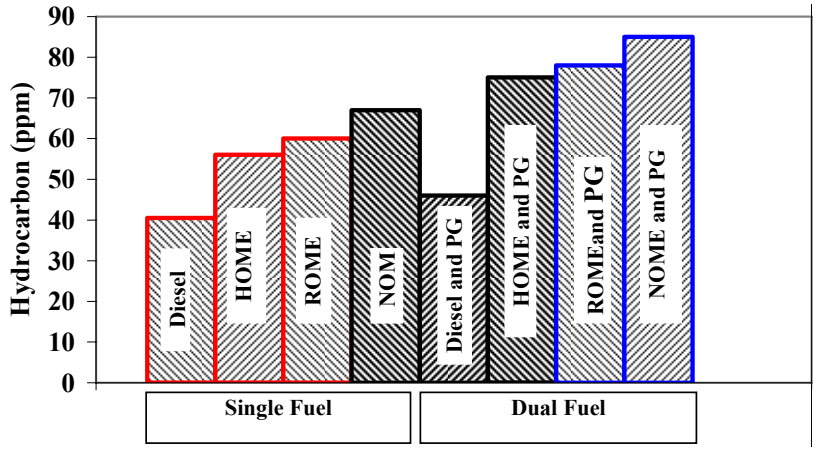

Figure 29. Variation of HC Emission with Different Modes of Engine Operation.

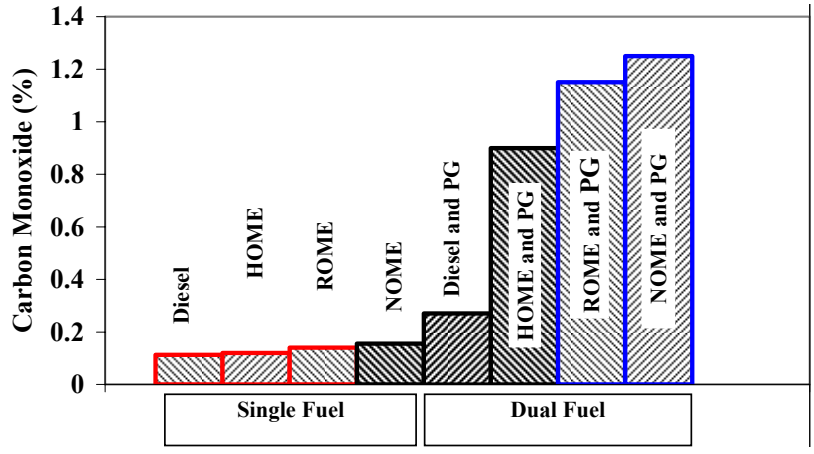

Figure 30. Variation of Carbon monoxide Emission with Different Modes of Engine Operation.

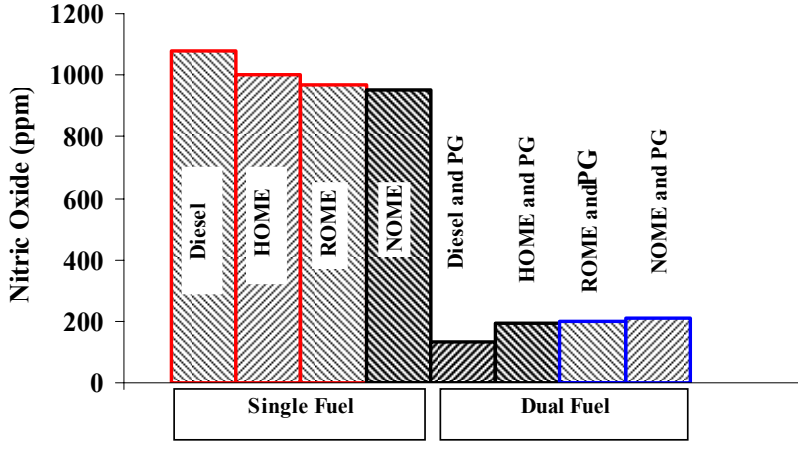

Figure 31. Variation of Nitric Oxide Emission with Different Modes of Engine Operation.

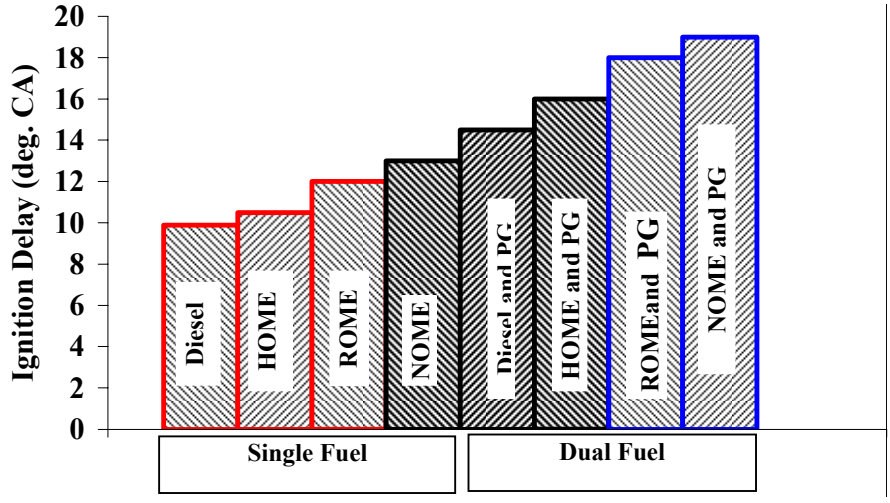

Figure 32. Variation of Ignition Delay with Different Modes of Engine Operation.

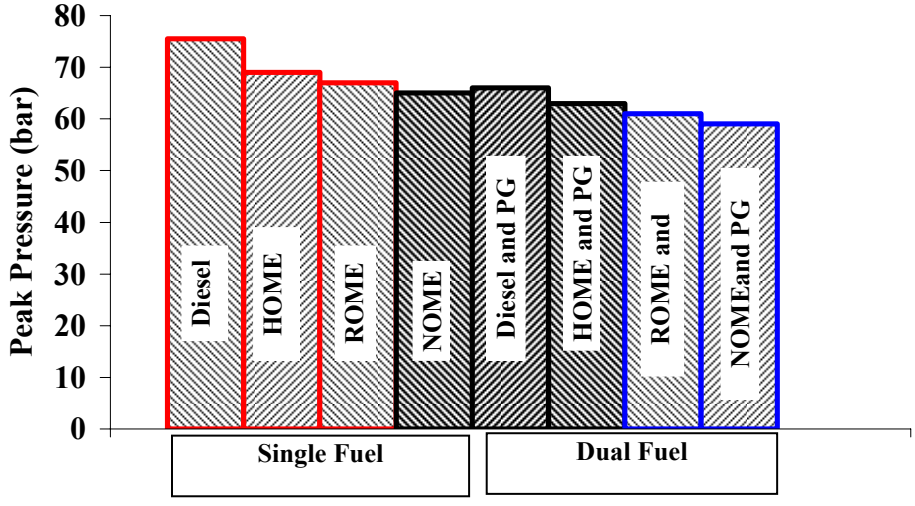

Figure 33. Variation of Cylinder Peak Pressure with Different Modes of Engine Operation.

Figure 32 shows variation of ignition delay with different modes of engine operation. Ignition delay of the injected fuels was found to increase in dual fuel mode of operation.

Figures 33 and 34 show variation of peak pressure and rate of pressure rise with different modes of engine operation. Rate of pressure rise is lower in dual fuel operation as compared to single fuel operation.

Figure 35 shows variation of combustion duration with different modes of engine operation. Dual fuel operation resulted in higher combustion duration compared to single fuel operations due to slower burning characteristic of the producer gas.

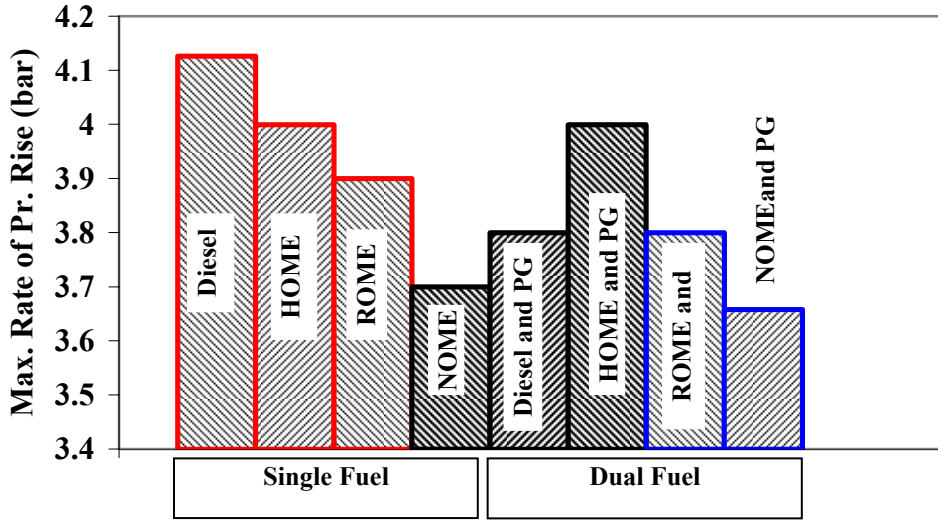

Figure 34. Variation of Maximum rate of pressure rise with Different Modes of Engine Operation.

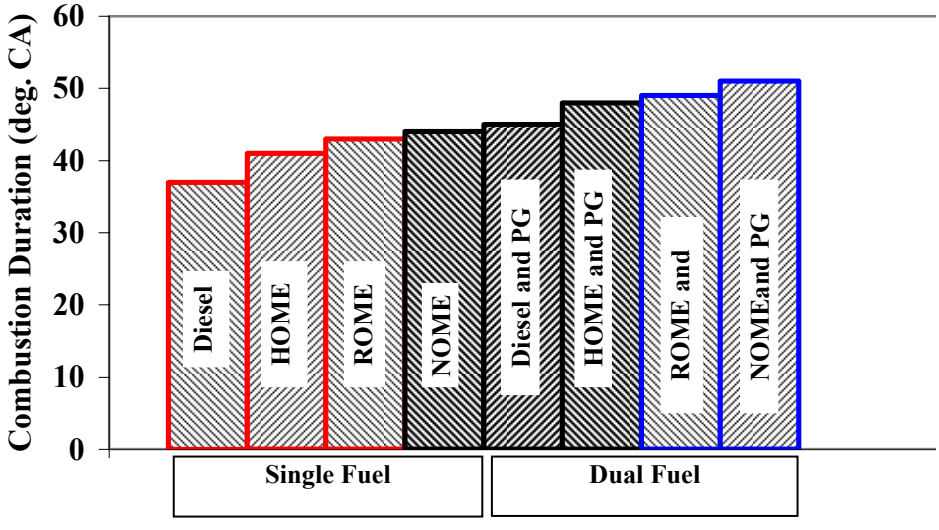

Figure 35. Variation of combustion duration with Different Modes of Engine Operation.

Figure 36 presents the fuel substitution for dual fuel operation at different power outputs. Fuel substitution values were maximum for diesel- Producer gas operation compared to vegetable oil combinations.

Injected fuel properties such as cetane number, viscosity and calorific value may be considered as responsible for the observed trend. The percentage of respective fuels substituted with Producer gas-diesel, Producer gas-HOME, Producer gas-NOME and Producer gas-ROME respectively were 71.00%, 54.00%, 64.50% and 50%.

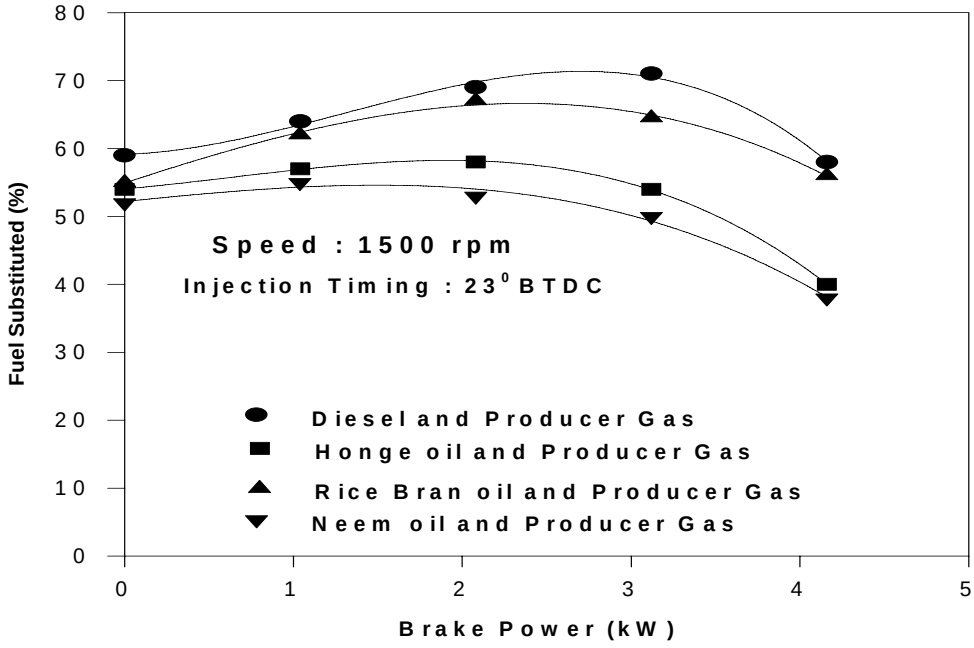

Figure 36. Variation of fuel substituted with brake power.

CONCLUSION

This work was aimed at studying performance, combustion and emission characteristics of a diesel engine operated on methyl esters of Honge, Rice Bran and Neem oils in single and in dual fuel mode with Producer gas induction. Based on the comprehensive experimental investigations carried out the following conclusions have been derived.

Transesterification of Non Edible Oils

- The quantity of catalyst and methyl alcohol used is crucial for successful reaction. Washing is necessary to drain away undesired contaminants in the biodiesel. The biodiesel should be finally heated to remove excess moisture.
- The optimum values of the parameters that result in highest biodiesel yield (98%) are 1% NaOH catalyst, 5:1 molar ratio of methyl alcohol, 60 minutes and 65 ^{o}C respectively. While for rice bran oil the reaction time was observed to be 180 minutes.
- The properties of HOME, ROME and NOME were comparable to that of standard diesel.

Experiments with Methyl Esters of Honge, Rice Bran and Neem Oils

For longer period of operation it is always better to operate the engine with ester oils than their crude form. The performance of HOME was better compared with ROME and NOME.

- Brake thermal efficiency of the engine improved by 6.00% with HOME compared to raw Honge oil operation.
- Reduction in smoke emission with reference to Honge oil is 13.00%.
- Reduction in HC and CO emissions with reference to Honge oil are 17.72% and 23.68%.
- Increase in NO emissions with reference to Honge oil is 26.92%. While decrease in NO emissions with reference to diesel is 9.00%
- With Honge oil methyl ester operation it is observed that the values of peak pressure, maximum rate of pressure rise and premixed heat release rate were higher compared to Honge oil operation. Also ignition delay and combustion duration were smaller compared to Honge oil operation.
- 19^0BTDC fuel injection timing was found to be optimum for Honge oil methyl ester operation.

Among the different esters tested, HOME gave the best performance with reduced emissions.

Experiments with HOME, ROME and NOME and Producer Gas in Dual Operation

The engine operated smoothly with all the selected combinations of fuels. In general a decrease in brake thermal efficiency and reduced engine emissions of smoke, HC, CO and NO_X were observed with increased CO emission.

- Dual fuel operation with HOME-Producer gas was better than Honge oil-Producer gas.
- The brake thermal efficiency of engine in dual fuel mode with producer gas operated with all the injected fuels such as diesel, HOME, ROME and NOME is found to be 24.25, 20.50, 19.00 and 17.80% respectively.
- The smoke opacity of 34.5 HSU, 57.5 HSU, 61.0 and 65.0 HSU were obtained with Producer gas-diesel, Producer gas- HOME, and Producer gas- ROME and Producer gas- NOME respectively. Nitrogen oxide emissions in dual fuel mode of operation were 130 ppm, 195 ppm 200 and 212 ppm with diesel, HOME, ROME and NOME as injected fuel respectively.
- HC / CO emissions of producer gas-injected fuels in dual fuel engine are found to be high.
- The exhaust gas temperature of 455, 485, 498 and 510^0C were observed with Producer gas-diesel, Producer gas- HOME, and Producer gas- ROME and Producer gas- NOME respectively
- The percentage of respective fuels substituted with Producer gas-diesel, Producer gas- HOME, and Producer gas- ROME and Producer gas- NOME respectively were 71.00%, 54.00%, 64.50% and 50%.

CLOSURE

On the whole it is concluded that HOME, ROME and NOME could be used as alternative fuels in diesel engines. Running the engine in dual fuel mode requires no major modifications in the existing engine. Renewable fuels like Producer gas- HOME, Producer gas- ROME and Producer gas- NOME are suitable for dual fuel operation and their extensive use will pave way for the energy security of the country.

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Chapter 13

BIOMASS GASIFIER BASED POWER PROJECTS UNDER CLEAN DEVELOPMENT MECHANISM IN INDIA: A PRELIMINARY ASSESSMENT

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ABSTRACT

Bio-energy accounts for about 14% of the global primary energy supply. Biomass is mostly being used in an inefficient manner in the rural areas of developing countries that leads to a host of adverse implications on human health, environment, and social well being. Therefore, the utilization of biomass in a clean and efficient manner to deliver modern energy services to the world's poor remains an imperative for the development community. One possible approach to do this is through the use of biomass gasifiers. Considerable efforts have been directed towards developing and deploying biomass gasifiers in many countries however, scaling up their dissemination remains an elusive goal.

So far, the cumulative capacity of biomass gasification projects in India is far below their theoretical potential despite government subsidy programmes. One of the major barriers is the high costs of investments in these systems. The Clean Development Mechanism (CDM) of the Kyoto Protocol (KP) provides Annex-I (industrialized) countries with an incentive to invest in emission reduction projects in non-Annex-I (developing) countries to achieve a reduction in CO_2 emissions at lowest cost that also promotes sustainable development in the host country. Biomass gasification projects could be of interest under the CDM because they directly displace greenhouse gas (GHG) emissions while contributing to sustainable rural development. However, there are only two biomass gasifier project registered under the CDM so far. In this chapter, an attempt has been made to assess the CO_2 mitigation potential of biomass gasifier based projects under CDM in India.

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The results indicate that in India around 74 million tonne agricultural residues as a biomass feedstock can be used for energy applications on an annual basis. In terms of the plant capacity the potential of biomass gasification projects could reach 31 GW that can generate more than 67 TWh electricity annually. The annual CER potential of biomass gasification projects in India could theoretically reach 58 million tonnes. Under more realistic assumptions about diffusion of biomass gasification projects based on past experiences with the government-run programmes, annual CER volumes by 2012 could reach 0.4 to 1.0 million and 1.0 to 3.0 million by 2020. The projections based on the past diffusion trend indicate that in India, even with highly favorable assumptions, the dissemination of biomass gasification projects is not likely to reach its maximum estimated potential in another 50 years. CDM could help to achieve the maximum utilization potential more rapidly as compared to the current diffusion trend if supportive policies are introduced.

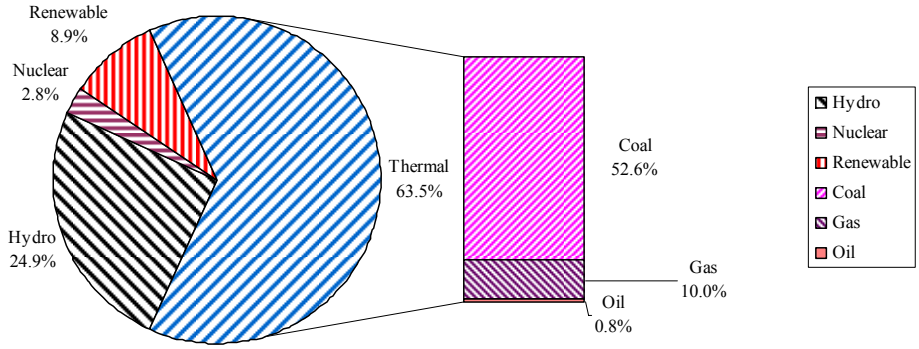
Keywords: clean development mechanism, biomass gasification, agricultural residues, India.

1. INTRODUCTION

Energy is a vital ingredient in economic development. With the increasing world population and the rising living standards, the global energy demand is steadily increasing (EIA, 2006). Moreover, developing countries are facing the challenge of sustaining economic growth, achieving social development and ensuring environmental protection (Beg et al., 2002). Therefore, the energy exploitation and utilization should be based on the sustainable development and better ecological environment in developing countries, so that we can attain the objective of coordinating the relationships among society, economy, energy and sustainable environment that meets the needs of the present without compromising the ability of future generations to meet their own needs (Dincer, 1998). The energy development programme of India has been put to severe pressure with the ever increasing demand supply gap and mismatch of resources coupled with non-uniform growth curve (Rajkumar, 2005). The challenges faced by India in the management and development of the power sector are multi-dimensional and they stem fundamentally from the increase in demand for energy due to rapid industrialization and growing population (Reddy and Balachandra, 2003), constraint of financial resources for enhancing this infrastructure facility (Ghosh, 2007), and limited reserves of coal and fossil fuels and consequent burden on foreign exchange due to increasing imports (Asif and Muneer, 2007). In response to these challenges, the energy policy of the country focuses on rapid development of all forms of energy, both conventional and non-conventional, promoting energy conservation and efficient management of demand, environment conservation and sustainable development, and development of decentralized energy systems based on renewable sources especially for use in rural areas (Mongia et al., 2001; Venkata et al., 2001; Jebaraj and Iniyan, 2006; Yang, 2006; Purohit, 2008).

The Government of India (GOI) is making conscious efforts to make substantial improvements to the electricity infrastructure in terms of availability and accessibility. Figure 1 presents the total installed capacity of power plants in India. The cumulative installed capacity of electric power plants in India under utilities was 148 GW till April 2009 of which contributions of hydro, thermal, nuclear and renewable sectors were 37, 94, 4 and 13GW,

respectively (http://powermin.nic.in). However, there is a supply-demand gap of 8 to 10% and peak load demand of 18 to 20% (Rajkumar, 2005). This has also accentuated by non-decentralized nature of power generation with vast area in the rural segment which are not connected by the grid for reliable and quality power. The Electricity Act, 2003 focuses on creating competition, protecting consumers, rationalizing tariffs and providing reliable power supply. It specifically encourages promotion of generation of electricity from renewable sources and directs the regulatory bodies to specify a percentage of total consumption of electricity from such sources. The GOI has also announced a programme for accelerated electrification of 0.1 million villages and 10 million households by the year 2012. This is expected to lead to 100% electrification at household level by the year 2012 (MNRE, 2008).

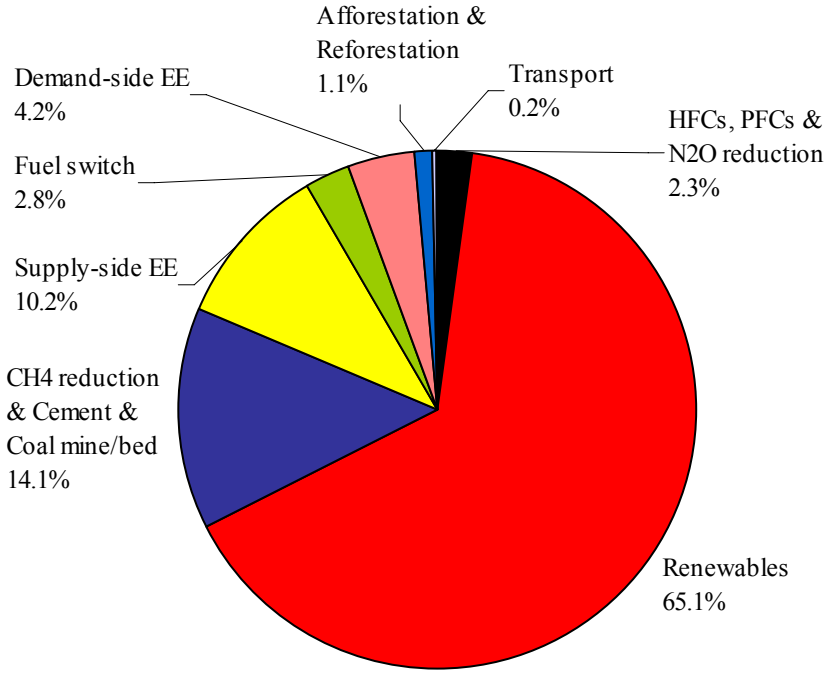


Source: (Central Electricity Authority, Ministry of Power, Government of India, New Delhi).

Figure 1. Electricity scenario of India as on April 31st 2009.

India is a tropical country blessed with abundant sunshine and rains, thus offering an ideal environment for biomass production. Further, the vast agricultural produce also makes available large quantities of agricultural residues which can be used to meet energy needs (Kumar et al., 2002). With an estimated production of about 350 million tonnes of agricultural waste every year, residual biomass is capable of mitigation of GHG emissions to the extent of 300 million tones per year (Rajkumar, 2005). The estimated potential of biomass power (agricultural residues) in India is more than 16,000 MW (MNRE, 2008) whereas the cumulative installed capacity of grid-interactive biomass power was only 683 MW till 1st January 2009 that is far below from their respective potential (www.mnre.gov.in). One of the possible barriers to the large-scale dissemination of biomass power projects in India is the high upfront cost of these systems (Purohit, 2009). Other barriers to the large-scale dissemination of biomass power projects are technical barriers, financial drawbacks, poor institutional framework, short-sighted electric utility policies, and low environmental concern, etc. (Rao and Ravindranath, 2002; Kishore et al., 2004; Parikka, 2004; Ghosh et al., 2006; Ravindranath et al., 2006). The Clean Development Mechanism (CDM) of the Kyoto Protocol allows developing countries to generate emission credits (Certified Emissions Reductions, CERs) for industrialized countries at lowest cost by greenhouse gas (GHG) emission reduction projects. Biomass gasification projects become relevant for the CDM because they directly displace GHG emissions while contributing to sustainable rural development. Out of the 4417 projects submitted to the CDM Executive Board (EB) until May 2009, 2877 (65%) projects are on renewables.

Figure 2 presents the percentage of CDM projects in each category until May 2009. 15% (645 projects) of the 4417 projects submitted to the CDM EB belong to biomass energy (www.unfccc.int). In this chapter, an attempt to assess the CDM potential of biomass gasification projects in India has been made before discussing whether at the current market situation such projects could become attractive.



Source: www.cd4cdm.org.

Figure 2. Percentage of CDM projects in each category.

The chapter is set out as follows. Section 2 provides some salient features of the Indian programme on biomass power. A brief detail of biomass gasifier technology is given in section 3. Section 4 presents the potential of biomass gasification projects in India. The discussion how the CDM could mobilize biomass gasification projects and the estimation of the CDM potential of biomass gasification projects is discussed in sections 5 and 6 respectively. Section 7 presents the forecast diffusion levels of biomass gasification projects under an optimistic CDM and business-as-usual scenario. Section 8 summarizes the findings of the study.

2. BIOMASS POWER PROGRAMME IN INDIA

Biomass power is an important alternative for providing energy in the rural sector (Hall, 1991). The Ministry of New and Renewable Energy (MNRE) of the GOI has been promoting productive and efficient utilization of biomass for energy generation realizing the enormous

potential for power generation available from biomass. The national programme on biomass power generation has been initiated by the GOI through the MNRE. It covers a) off-grid power projects for meeting unmet demand of electricity in electrified villages; and b) grid interactive MW level power project with 100% producer gas engine with the objective to meet the unmet demand of electricity in villages, demonstration projects (for 100% producer gas engine) coupled with gasifier for off grid and grid power operation, and to support and thus enlarge activities, through awareness creation, publicity measures, seminars/workshops/ business meets/ training programme etc. The programme is being implemented through State Nodal Agencies (SNAs) with the involvement of Energy Service Companies (ESCOs), Cooperative, Panchayats, NGOs, manufactures or entrepreneurs etc.

The MNRE has been providing support for promoting development and deployment of biomass resources through combustion, gasification and co-generation technologies for power generation (captive, off-grid and grid connected) and also for thermal applications (MNRE, 2008). For example, the MNES has been supporting development and deployment of biomass gasifiers for almost two decades. As a result, a variety of biomass gasifier based power generation systems of capacities varying in the range of 5–1000 kWe have been developed indigenously. Most of the biomass gasification systems for electricity generation installed up to 2002–2003 were based on dual-fuel engine technology. In recent years installation of biomass gasifier systems equipped with engines operating on 100% producer gas has also been taken up. The cumulative installed capacity of biomass gasifier systems (including both dual fuel as well as 100% producer gas mode systems) with aggregate capacity of 160 MWe have been deployed until January 2009 in the country under the programme implemented by the MNRE (www.mnre.gov.in). Under its programme on biomass gasifiers, the MNRE is providing capital subsidy to the users for installation of biomass gasifiers. The amount of capital subsidy on pro-rata basis during 2006–2007 is to the extent of Rs. 1.5 million for a basic package of a 100 kW biomass gasification projects covering housing for system and local electricity distribution network for electricity generation (MNRE, 2008). The central financial assistance (CFA) is routed through SNAs.

3. BIOMASS GASIFIER TECHNOLOGY

Biomass can be utilized through three different processes for energy conversion: gasification, pyrolysis and direct combustion (Bridgwater et al., 2002). Gasification is the thermo-chemical process of obtaining energy from solid matter in a gaseous form (Ravindranath, 1993). In principle, the process is a thermal decomposition of organic matter in the presence of limited supply of air or oxygen to produce combustible gases thus converting calorific value of organic material into a gaseous energy carrier (Ravindranath and Hall, 1995; Tripathi et al., 1997). In contrast to complete combustion of solid carbonaceous material, the process of pyrolysis refers to combustion in a deficient supply of air/oxygen (Ganesh and Banerjee, 2001). The process gives out carbon-mono-oxide and methane, which are condensed to form tar and aqueous liquor. The latter is then distilled to give methanol and other organic substances. In direct combustion, thermal decomposition of organic matter is carried out in the presence of excess air, liberating heat and leaving behind incombustible ash (Fuel + Air → Heat + Ash + Inert Gases). Direct combustion of biomass is an important route

for generation of grid-quality power by efficient use of agricultural, agro-industrial and forest residues, which are either being wasted or are being sub-optimally utilized in the country. Among all biomass conversion processes, gasification is one of the promising ones as the energy efficiency in case of gasification is higher than that of combustion (Devi et al., 2003).

A biomass-gasifier-based power generation system normally consists of a biomass-gasifier, a gas cooling and cleaning unit, and a dual-fuel-engine-electrical generator as shown in Figure 3. Design of gasifier depends upon type of fuel used and whether gasifier is portable or stationary.

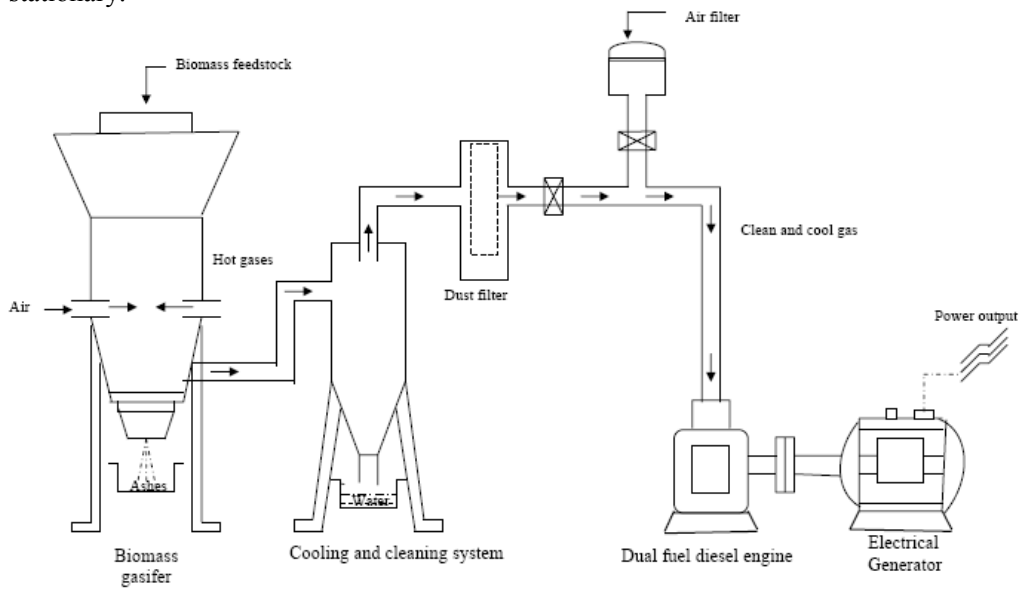


Figure 3. Schematic diagram of a biomass-gasifier-based power generation system.

In Indian market, generally downdraft gasifiers are available due to utilization of mechanical mode. The biomass-gasifier is usually a cylindrical unit with a conical combustion chamber made of mild steel. Biomass preparation unit is used to cut the collected biomass to proper size for feeding into the biomass gasifier. Once fed into the gasifier biomass undergoes drying, pyrolysis, oxidation and reduction reactions in a limited supply of air to produce a combustible mixture of carbon monoxide, hydrogen and methane; diluents viz. carbon dioxide and nitrogen; and tar and ash (Tripathi et al., 1997). The biomass is fed from the top and its gasification takes place under controlled thermal conditions. The gaseous product of biomass gasification is known as 'producer gas', which is passed through a cooling and cleaning unit before feeding into the diesel engine. The cooling and cleaning unit consists of a scrubber and a separate box with a cloth filter. Tar and ash are removed in the cooling and cleaning unit of the gasifier system as they affect the operation and performance of engine adversely. The scrubber mainly cools the gas and removes coarse particulates, and the fine dust particulates are removed through a filter in a separate box. The clean and cool gas is mixed with air before entering the engine-generator unit to produce electricity. About 65-70% of the diesel may be replaced by the producer gas in a diesel engine operating in a dual-fuel mode (Ravindranath and Hall, 1995). In dual fuel mode operation of engine, diesel or bio-diesel can be used as pilot fuel and producer gas is used as the main fuel but in 100% producer gas mode of operation an appropriate provision is to be made for initiating

combustion. Use of locally produced bio-diesel as pilot fuel can completely eliminate dependence on diesel especially in remote locations, where transportation of diesel itself may be a difficult task. The electricity generated through the biomass gasifier based power project is distributed to the consumers through a local mini-grid.

For biomass gasification projects, two potential risks viz. technological and financial risks are possible. Uncertainties in gasifiers and/or system performance constitute to the technological risks whereas uncertainties in the recovery of user charges in the absence of the mechanisms constitutes the financial risk. For example, tar formation due to the pyrolysis of biomass. The increase in moisture content of the biomass would increase the tar formation. In case of coconut shell as a biomass feedstock, if the moisture is less than 15% the tar content will be in the range of 50-250 mg/Nm^3 and the increase in moisture level will increase the tar content to 700 mg/Nm^3. The tar formation level is very low in downdraft gasifier as compared to up draft gasification even though it requires fine cooling and cleaning system to reduce the quantity of tar, particulate matter and moisture in the gas before supplied to the engine (Dogru et al., 2002; Zainal et al., 2002; Kumabe et al., 2007). Several approaches for tar reduction have been reported in the literature (Bhattacharya et al., 2001; Devi et al., 2003; Zhang et al., 2004; Devi et al., 2005). The tar content of the producer gas can be reduced by the increase of the airflow rate. Bhattacharya et al. (2001) observed that for a relatively high rate of primary air supply tar content in producer gas is low due to the higher reactor temperature levels and longer residence time of tar vapor in the gasifier. Catalytic hot gasification gas cleaning is another interesting and promising method for tar elimination (Pfeifer and Hofbauer, 2008).

The cooling and cleaning of producer gas is another major barrier for this technology. There is always a constriction at the level of the oxidation zone to force the pyrolysis products through a concentrated high temperature zone to achieve complete decomposition. This concentrated oxidation zone can cause sintering or slagging of ash resulting in clinker formation and consequent blocking of the constricted area and/or channel formation. Continuous rotating ash grates or other mechanical shaking may be required to avoid this problem. Bhave et al. (2008) developed the producer gas cooling–cleaning unit, in which the gas cooling and cleaning take place effectively in one vertical tower, unlike other systems which have several chambers for these tasks. It is easy to operate, and has a low pressure drop. The unit will give a clean gas with 'tar and dust' content below the limit of 150 mg/nm^3 as long as the inlet gas 'tar and dust' content is below about 600 mg/nm^3. Moreover, handling of producer gas in large quantities is very dangerous owing to the large inflammability limit of carbon monoxide ranging from 5-74%. Gas tight solid handling, continuous feeding is very difficult in gasification system and needs more operator attention. Similarly, the financial risk due to the erratic increase in the price of biomass is possible that is attributed to the expected increase in price of biomass transportation cost due to increase in diesel price.

4. TECHNICAL POTENTIAL OF BIOMASS GASIFICATION PROJECTS IN INDIA

Agricultural residues are the most commonly used biomass feedstocks for biomass gasification projects in India (Tripathi et al., 1998). Table 1 presents some of the alternative uses of agricultural residues along with the agricultural residue availability (kg) per tonne of

grain produced based on the available data on residue to crop ratio (NPC, 1987). It may be noted that wheat straw is used as cattle feed in rural India. Paddy straw is used as domestic fuel, as cattle feed, in manufacturing straw board, as a raw material for paper and hardboard units, as packing material for glasswares, etc. (Purohit et al., 2006). Similarly, bagasse is mostly used for meeting the thermal energy requirement of sugar mills. Therefore, in this study these agricultural residues have not been considered for the estimation of the utilization potential of biomass gasification projects within the country. Table 2 presents the annual production of different crops in India considered in this study (MOA, 2003).

Table 1. Agricultural residue availability (in kg) per tonne of grain produced and its alternative uses

Crop	Crop-residue	Crop to residue ratio	Agricultural residue availability (in kg) per tonne of grain produced	Alternative uses
Groundnut	Groundnut shell	0.33	330	Domestic fuel*, cattle feed
Wheat	Wheat straw	1.47	1470	Cattle feed
Paddy	Rice husk	0.33	330	Domestic fuel, cattle feed, construction materials etc.
	Paddy straw	1.53	1530	Domestic fuel, cattle feed, construction materials, manufacturing straw board, raw material for paper and hardboard units, packing material for glasswares, etc.
Sugarcane	Bagasse	0.25	250	Energy feedstock in sugar mills, Paper and pulp industry
Cotton	Cotton stalk	3.00	3000	Domestic fuel
Arhar	Arhar stalk	1.32	1320	Domestic fuel
Corn	Corn cobs	0.30	300	Domestic fuel
	Corn stalks	1.56	1560	Cattle feed, Domestic fuel
Jute	Jute sticks	2.30	2300	Domestic fuel
Mustard	Mustard stalks	1.85	1850	Domestic fuel

*Domestic fuel for cooking, water heating and space heating.
Source: (NPC, 1987).

Availability of agricultural residues as energy feedstock essentially depends upon the total amount of crop produced, residue to crop ratio for the crop, collection efficiency (which also includes storage-related considerations), and amount used in other competing applications. The effective crop residue availability for i^{th} crop ($CRA_{eff,i}$) per unit crop produced can therefore be expressed as (Purohit et al., 2006)

$$CRA_{eff,i} = RC_i \left(1-\alpha_i\right)\left(1-\beta_i\right) \quad (1)$$

where RC_i represents the residue to crop ratio for i^{th} crop, α_i the fraction of the total crop-residue lost in collection, transportation, storage etc., and β_i the fraction of remaining crop residues used in other competing applications.

Table 2. All India production of different crops considered in this study

State	Annual production (million tones)							
	Rice	Maize	Arhar	Groundnut	Cotton[1]	Jute and Mesta	Mustard and Rapeseeds	Coconut[2]
Andhra Pradesh	11.45	1.43	0.22	2.03	1.66	0.69	NA	10.93
Assam	4.00	NA	NA	NA	NA	0.69	0.14	1.36
Bihar	5.42	1.46	0.06	NA	NA	1.30	0.10	NA
Chhattisgarh	3.24	NA	NA	NA	NA	NA	NA	NA
Goa	NA	NA	NA	NA	NA	NA	NA	1.25
Gujarat	1.01	0.62	0.11	0.69	1.16	NA	0.23	NA
Haryana	2.68	NA	NA	NA	1.38	NA	0.55	NA
Himachal Pradesh	0.68	NA	NA	NA	NA	NA	NA	NA
Jammu and Kashmir	NA	0.53	NA	NA	NA	NA	NA	NA
Jharkhand	1.64	0.11	0.03	NA	NA	NA	NA	NA
Karnataka	3.73	2.11	0.26	0.90	0.98	NA	NA	17.54
Kerala	0.75	NA	NA	NA	NA	NA	NA	54.96
Madhya Pradesh	0.96	1.20	0.23	0.24	0.24	NA	0.36	NA
Maharashtra	1.95	0.22	0.66	0.46	1.80	0.04	NA	2.44
Meghalaya	NA	NA	NA	NA	NA	0.05	NA	NA
Orissa	4.61	NA	0.08	0.06	NA	0.14	NA	1.1
Punjab	9.15	0.46	NA	NA	1.20	NA	0.07	NA
Rajasthan	NA	1.01	NA	0.18	0.81	NA	1.31	NA
Tamil Nadu	7.22	0.19	0.06	1.46	0.33	NA	NA	31.58
Uttar Pradesh	11.54	1.49	0.5	0.10	NA	NA	0.90	NA
West Bengal	12.43	0.09	NA	NA	NA	7.51	0.42	3.31
Others	3.09	0.47	0.05	0.10	0.09	0.06	0.13	1.5
All India	85.55	11.39	2.26	6.22	9.65	10.48	4.21	125.97

[1]million bales; [2]00, million nut; NA: Not available.

Source: MOA (2003).

Therefore, the effective gross annual crop residues availability, GRA_{eff}, for energy applications in India can be estimated as

$$GRA_{eff} = \sum_{i=j=1}^{m,n} A_{i,j} Y_{i,j} RC_i \left(1-\alpha_i\right)\left(1-\beta_i\right) \quad (2)$$

where $A_{i,j}$ and $Y_{i,j}$ respectively represent the area and yield of i^{th} crop (i = 1, 2, 3, … m crop) in the j^{th} ((i = 1, 2, 3, … n state)) state.

If the effective gross annual crop residues available for energy application in India can be diverted through the biomass gasification route for power generation, then the potential of biomass gasification projects (in terms of the plant capacity) can be estimated as

$$P_{bg} = \left(\frac{1}{8760\, CUF_{bg}\, s_{bc}}\right) \sum_{i=j=1}^{m,n} A_{i,j} Y_{i,j} RC_i \left(1-\alpha_i\right)\left(1-\beta_i\right) \quad (3)$$

where CUF_{bg} represents the capacity utilization factor of the biomass gasifier based power project and s_{bc} the specific biomass consumption in biomass gasification route.

Table 3 presents the potential availability of agricultural residues for energy applications of select crops in different states. For the estimates presented in Table 3, the fraction of the total amount of agricultural residues lost in collection, transportation and storage, etc. has been assumed as 0.10 (NPC, 1987) and the fraction of remaining amount of agricultural residues used in other competing applications has been taken as 0.15 (Purohit et al., 2006). The effective availability of agricultural residue for energy application is highest in the southern (Kerala, Andhra Pradesh, Tamilnadu etc.) states as compared to the northern states (Punjab, Haryana, Uttar Pradesh, Rajasthan etc.) of the country. The highest production of agricultural residues in the southern states of the country can be attributed to the fact that the production of non-fodder, non-fertilizer agricultural residues is highest in these states as compared to the northern states. The all India annual potential availability of agricultural residues for energy applications in different states of India has been estimated as 74 million tonne on annual basis (see Table 3).

The specific biomass consumption in the dual-fuel mode of operation of a biomass gasifier based system essentially depends on a number of factors such as type of biomass, its moisture content and calorific value, operating load on biomass gasifier based system, diesel replacement factor, etc. and is estimated to be in the range of 1.0–1.4 kg/kWh for operation at the rated capacity of biomass gasifier based power project (Tripathi et al., 1997; Mukhopadhyay, 2004; Nouni et al., 2007). Average fuel wood consumption per kWh of electricity generated has been reported as 0.822 kg for the 5-100 kW biomass gasification projects installed in Gosaba Island of Sundarbans, West Bengal (Ghosh et al., 2006). Therefore, considering wide variations in reported values of specific biomass consumption (0.822–1.4 kg/kWh) in the present study specific biomass consumption at rated capacity of biomass gasification project have been considered as 1.1 kg/kWh. Similarly, a capacity utilization factor of 25% (i.e. CUF_{bg} = 0.25) has been considered in this study. Table 4 presents the estimated potential of biomass gasification projects in different states of India (in

Table 3. Annual potential availability of agricultural residues for energy applications in different states of India

State	Agricultural residues (million tonne)									
	Rice husk	Maize cobs	Maize stalks	Arhar stalk	Groundnut shells	Cotton stalk	Jute and Mesta sticks	Mustard stalk	Coconut coir	Total
• Andhra Pradesh	• 2.89	• 0.33	• 1.71	• 0.22	• 0.51	• 0.65	• 0.22	• NA	• 1.67	• 8.20
• Assam	• 1.01	• NA	• NA	• NA	• NA	• NA	• 0.22	• 0.20	• 0.21	• 1.63
• Bihar	• 1.37	• 0.34	• 1.74	• 0.06	• NA	• NA	• 0.41	• 0.14	• NA	• 4.06
• Chhattisgarh	• 0.82	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• 0.82
• Goa	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• 0.19	• 0.19
• Gujarat	• 0.25	• 0.14	• 0.74	• 0.11	• 0.17	• 0.45	• NA	• 0.33	• NA	• 2.20
• Haryana	• 0.68	• NA	• NA	• NA	• NA	• 0.54	• NA	• 0.78	• NA	• 1.99
• Himachal Pradesh	• 0.17	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• 0.17
• Jammu and Kashmir	• NA	• 0.12	• 0.63	• NA	• NA	• NA	• NA	• NA	• NA	• 0.75
• Jharkhand	• 0.41	• 0.03	• 0.13	• 0.03	• NA	• NA	• NA	• NA	• NA	• 0.60
• Karnataka	• 0.94	• 0.48	• 2.52	• 0.26	• 0.23	• 0.38	• NA	• NA	• 2.68	• 7.50
• Kerala	• 0.19	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• 8.41	• 8.60
• Madhya Pradesh	• 0.24	• 0.28	• 1.43	• 0.23	• 0.06	• 0.09	• NA	• 0.51	• NA	• 2.85
• Maharashtra	• 0.49	• 0.05	• 0.26	• 0.67	• 0.12	• 0.70	• 0.01	• NA	• 0.37	• 2.68
• Meghalaya	• NA	• NA	• NA	• NA	• NA	• NA	• 0.02	• NA	• NA	• 0.02
• Orissa	• 1.16	• NA	• NA	• 0.08	• 0.02	• NA	• 0.04	• NA	• 0.17	• 1.47
• Punjab	• 2.31	• 0.11	• 0.55	• NA	• NA	• 0.47	• NA	• 0.10	• NA	• 3.53
• Rajasthan	• NA	• 0.23	• 1.21	• NA	• 0.05	• 0.32	• NA	• 1.85	• NA	• 3.65
• Tamil Nadu	• 1.82	• 0.04	• 0.23	• 0.06	• 0.37	• 0.13	• NA	• NA	• 4.83	• 7.48
• Uttar Pradesh	• 2.91	• 0.34	• 1.78	• 0.50	• 0.03	• NA	• NA	• 1.27	• NA	• 6.84
• West Bengal	• 3.14	• 0.02	• 0.11	• NA	• NA	• NA	• 2.38	• 0.59	• 0.51	• 6.75
• Others	• 0.78	• 0.11	• 0.56	• 0.05	• 0.03	• 0.04	• 0.02	• 0.18	• 0.23	• 1.99
• All India	• 21.60	• 2.61	• 13.59	• 2.28	• 1.57	• 3.76	• 3.32	• 5.96	• 19.27	• 73.97

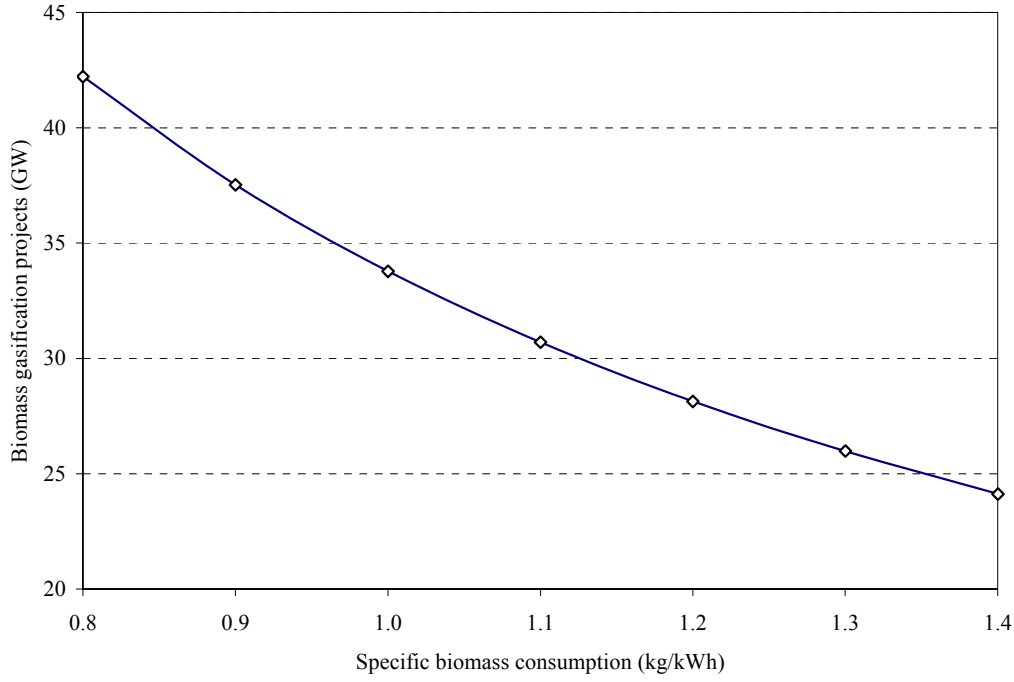
Source: own estimates.

Table 4. Estimated potential of biomass gasification projects in different states of India (in MW)

State	Estimated potential of biomass gasification projects (MW)									
	Rice husk	Maize cobs	Maize stalks	Arhar stalk	Groundnut shells	Cotton stalk	Jute and Mesta sticks	Mustard stalk	Coconut coir	Total
• Andhra Pradesh	• 1200	• 136	• 708	• 92	• 213	• 269	• 91	• NA	• 694	• 3403
• Assam	• 419	• NA	• NA	• NA	• NA	• NA	• 91	• 82	• 86	• 679
• Bihar	• 568	• 139	• 723	• 25	• NA	• NA	• 171	• 59	• NA	• 1685
• Chhattisgarh	• 340	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• 340
• Goa	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• 79	• 79
• Gujarat	• 106	• 59	• 307	• 46	• 72	• 188	• NA	• 135	• NA	• 913
• Haryana	• 281	• NA	• NA	• NA	• NA	• 223	• NA	• 323	• NA	• 827
• Himachal Pradesh	• 71	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• 71
• Jammu and Kashmir	• NA	• 50	• 263	• 0	• NA	• NA	• NA	• NA	• NA	• 313
• Jharkhand	• 172	• 10	• 54	• 13	• NA	• NA	• NA	• NA	• NA	• 249
• Karnataka	• 391	• 201	• 1045	• 109	• 94	• 159	• NA	• NA	• 1114	• 3113
• Kerala	• 79	• NA	• NA	• NA	• NA	• NA	• NA	• NA	• 3491	• 3569
• Madhya Pradesh	• 101	• 114	• 594	• 96	• 25	• 39	• NA	• 211	• NA	• 1181
• Maharashtra	• 204	• 21	• 109	• 277	• 48	• 292	• 5	• NA	• 155	• 1111
• Meghalaya	• NA	• NA	• NA	• NA	• NA	• NA	• 7	• NA	• NA	• 7
• Orissa	• 483	• NA	• NA	• 34	• 6	• NA	• 18	• NA	• 70	• 611
• Punjab	• 959	• 44	• 228	• NA	• NA	• 194	• NA	• 41	• NA	• 1466
• Rajasthan	• NA	• 96	• 500	• NA	• 19	• 131	• NA	• 770	• NA	• 1516
• Tamil Nadu	• 757	• 18	• 94	• 25	• 153	• 53	• NA	• NA	• 2006	• 3106
• Uttar Pradesh	• 1209	• 142	• 738	• 210	• 10	• NA	• NA	• 529	• NA	• 2838
• West Bengal	• 1303	• 9	• 45	• NA	• NA	• NA	• 987	• 247	• 210	• 2800
• Others	• 324	• 45	• 233	• 21	• 10	• 15	• 8	• 76	• 95	• 827
• All India	• 8965	• 1085	• 5643	• 947	• 652	• 1563	• 1378	• 2473	• 8001	• 30707

Source: own estimates.

MW). The results presented in this table indicate that if the net available agricultural residue for energy applications to be diverted in the gasification process then the annual potential of biomass gasifier based power project could reach around 31,000 MW. Figure 4 presents the results of a sensitivity analysis undertaken to study the effect of the specific biomass consumption on the biomass gasification potential of agricultural residues considered in this study. As expected, the theoretical potential of biomass gasification projects decreases with an increase in the specific biomass consumption in the biomass gasification unit.



Source: Own estimates.

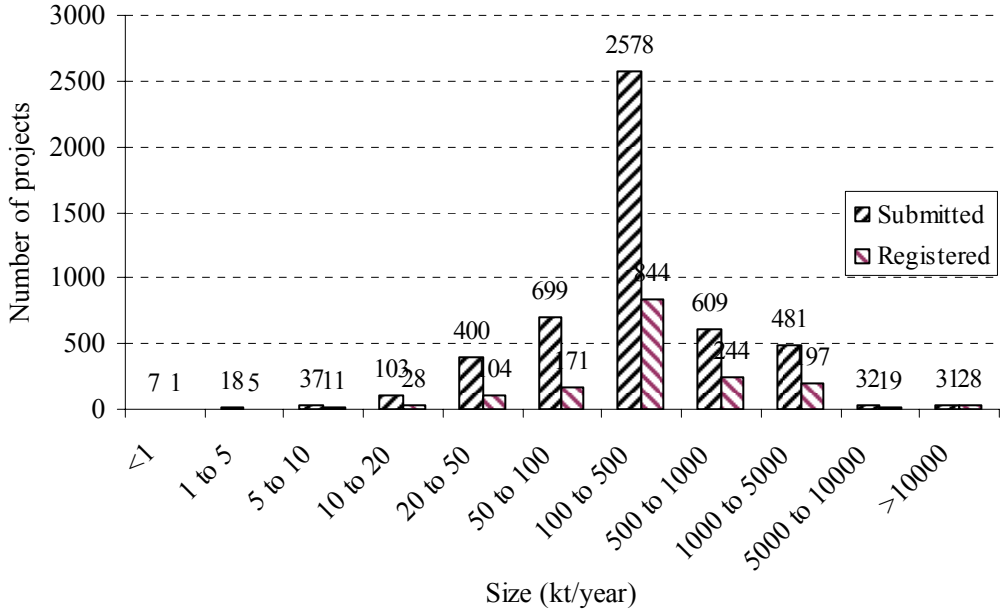
Figure 4. Effect of specific biomass consumption on the estimated potential of biomass power projects.

5. How the CDM Could Be Applied to the Large-Scale Dissemination of Biomass Gasification Projects?

Small-scale renewable energy and energy efficiency projects are helping to meet the needs of rural people in developing countries, alleviating poverty and fostering sustainable development. However, the low emission reductions per installation are making it difficult for such projects to derive value from participating in the CDM. Negotiators of the Marrakesh Accords of November, 2001 (UNFCCC, 2002) as well as the CDM Executive Board (EB) recognized this problem and adopted simplified CDM modalities and procedures for qualifying small-scale projects defined as a) renewable energy project activities with a maximum output capacity equivalent of up to 15 MW[2], b) energy efficiency improvement

[2] If the unit added has both renewable and non-renewable components (e.g.. a wind/diesel unit), the eligibility limit of 15MW for a small-scale CDM project activity applies only to the renewable component.

project activities which reduce energy consumption by an amount equivalent to 60 GWh per year, and c) other project activities whose emission reductions are less than 60 kt CO_2 per year. The thresholds for the latter two categories were increased by decision of the 12th Conference of Parties (COP-12) to the UNFCCC in November 2006. However, the current design of the CDM is resulting in high transactions costs to individual small-scale projects (Michaelowa and Jotzo, 2005) even with the simplified rules. Costs can be reduced by bundling similar small projects into a single project that is still eligible for the simplified procedures. The "gold rush" atmosphere of 2005 has also mobilized small scale project developers.



Source: CDM.UNFCCC.int and own estimates.

Figure 5. Size categories of submitted and registered CDM projects (average 1000 CERs p.a. until end of 2012).

Figure 5 shows the number of different project size categories of the 4417 CDM projects submitted until 1st June, 2009 (http://cdm.unfccc.int/index.html) of which 1652 projects have been registered by the CDM EB and 91 projects were requesting registration (http://unfccc.int). Out of the 1652 projects registered by the EB, 428 projects were located in India. However, only two projects "Bundle of 100 village biomass gasifier based power plants totalling 5.15 MW" by Decentralised Energy Systems India Pvt. Ltd. in Bihar and "Biomass gasification based power generation" by Arashi Hi-Tech Bio-Power Private Limited in Tamilnadu on biomass gasification are registered so far by the CDM EB. 4 CDM projects from India on biomass gasification were at the validation stage.

5.1. Baseline

The 'reference case' is the energy supply scenario used to define the baseline[3] situation for calculating the GHG emissions that would be expected in the absence of the installation of biomass gasification projects. The selection of the reference case will have a big impact on the amount of emission reductions that can be credited to the installation of biomass gasification projects. The CO_2 emissions mitigation benefits associated with a biomass gasifier based power project depend upon the amount of electricity and/or diesel saved. To estimate the CDM potential of biomass gasification projects in the country the small scale methodology AMS-I.D. "Grid connected renewable electricity generation" in its version of 23rd December 2006 (UNFCCC, 2006) has been used which explicitly mentions biomass power for electricity generation. For grid connected biomass gasification projects the baseline is the kWh produced by the biomass gasifier unit multiplied by an emission coefficient (measured in kg CO_2equ/kWh) calculated in a transparent and conservative manner. As per the small scale methodology AMS-I.D for a system where all generators use exclusively fuel oil and/or diesel[4] fuel, the baseline is the annual kWh generated by the renewable unit times an emission coefficient for a modern diesel generating unit of the relevant capacity operating at optimal load. For all other systems, the baseline (measured in kg CO_2e/kWh) calculated in a transparent and conservative manner as: (a) a combined margin (CM), consisting of the combination of operating margin (OM) and build margin (BM) according to the procedures prescribed in the approved methodology ACM0002[5], or (b) the weighted average emissions (in kg CO_2e/kWh) of the current generation mix.

5.2. Additionality

To maintain the environmental integrity of the Kyoto Protocol, CERs are given only for "additional" activities that would otherwise not be expected to occur. The 'additionality' criterion for the CDM is a key to ensure that CDM projects lead to real and additional emission reductions. Therefore, any CDM project requires careful analysis of additionality which has probably been the most contentious point in the development of the CDM and also resulted in great confusion amongst project developers (Sugiyama and Michaelowa, 2001; Shrestha and Timilsina, 2002; Greiner and Michaelowa, 2003). A number of different approaches, including those based on financial, barrier and market-penetration criteria have been suggested as a test for additionality. Carter (1997) and Beuermann et al. (2000) have proposed qualitative definitions whereby project developers need to describe and show specific barriers for CDM projects that do not exist for business-as-usual (BAU) cases, with the existence of these barriers implying that projects are 'additional', and not yet commercial

[3] The quantification of climate benefits of a project - i.e. the mitigation of GHG-emissions - is done by means of a "baseline". A baseline describes the (theoretical) emissions that would have occurred in case the CDM project was not implemented. The amounts of CERs that can be earned by the project are then calculated as the difference of baseline emissions and project emissions.

[4] A conversion factor of 3.2 kg CO2 per kg of diesel has been used (following revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories).

[5] Any of the four procedures to calculate the operating margin can be chosen, but the restrictions to use the Simple OM and the Average OM calculations must be considered

(see: Mathur et al., 2007). Greiner and Michaelowa (2003) have suggested assessing financial indicators (such as IRR, NPV, etc.) of proposed projects against threshold benchmarks or reference BAU projects.

The Kyoto Protocol stops short of requiring project proponents to show strict financial additionality - that the CDM revenue makes an uneconomic project economic – and left scope for the CDM EB to refine the demonstration of additionality. The EB subsequently took a fairly strict interpretation of additionality and developed an additionality tool which formally is voluntary but which has become de facto mandatory as it was incorporated in most baseline methodologies. The additionality tool requires an investment analysis and/or a barrier analysis to determine whether the CDM project is the most attractive realistic alternative. This means that the project can be profitable and additional as long as developers can show that another project type was even more profitable. However, concerns have been raised with methods currently used, such as investment analysis, barrier analysis, and performance thresholds. They have been variously critiqued for high costs, resistance to standardization, weak environmental integrity, and susceptibility to gaming. Kartha et al. (2005) suggest use of market penetration rates for determining the additionality of technologies used in CDM projects. Mathur et al. (2007) proposed a test for additionality that draws on the framework of the diffusion of innovations, especially the risk profile of adopters of new technologies or innovations. This approach has the potential to streamline the assessment for additionality, although it will require data on the rate of implementation of specific technologies or innovations.

Fuel supply plays a crucial role in determining the financial viability and sustainability of biomass gasifier projects. Competition with food produce makes biomass a potentially contentious fuel supply, precluding the dedicated use of existing farmland for biomass production (Ravindranath et al. 2005). For small-scale electrification, particularly community loads in rural areas, biomass gasification represent a sustainable and relatively low cost option for fulfilling basic electricity needs. Past studies have put the typical unit cost of electricity generation between Rs 2.5/kWh and Rs 7.5/kWh, with cost sensitive to load factor and fuel availability (Tripathi et al. 1997; Banerjee 2006; Nouni et al. 2007). As compared to the current electricity tariff of Rs 3-5/kWh, Cust et al. (2007) observed the unit cost of electricity generation between Rs 6-8/kWh for biomass gasifier based power projects in India. An analysis of the 6 projects on biomass gasification submitted from India is presented in Table 5. It may be noted that most of the project proponents experienced investment, technology and prevailing practice barriers. None of the project design documents (PDD's) provide investment analysis. Only one project submitted by Sri Gomathy Mills clearly mentioned the impact of CDM registration (see Table 5).

5.3. Monitoring

Monitoring shall consist of metering the electricity generated by the renewable technology. For a grid connected renewable energy project, emission reduction quantity totally depends on the units wheeled to the grid. The approved consolidated baseline methodology ACM0002 covers the monitoring of units wheeled along with the other

Table 5. Additionality test of Indian projects on biomass gasification

Title	Methodology	Investment Analysis	Barrier Analysis	Prevailing practice barrier	Identification of alternatives	Institutional /Regulatory Barriers	Technology Barriers	Common Practice Analysis	Impact of CDM registration	Remarks
9 biomass gasifier based power plants totaling 2.25 MW	AMS-I.A. + AMS-I.D.	X	√ PPB	√	X	√	X	X	X	Prevailing practice or existing regulatory or policy requirements would have led to implementation of a technology with higher emissions
5 Biomass gasifier based power plants totaling around 2 MW	AMS-I.A. + AMS-I.D.	X	√ PPB	√	X	√	X	X	X	Prevailing practice or existing regulatory or policy requirements would have led to implementation of a technology with higher emissions

Table 5. (Continued)

Title	Methodology	Investment Analysis	Barrier Analysis	Prevailing practice barrier	Identification of alternatives	Institutional /Regulatory Barriers	Technology Barriers	Common Practice Analysis	Impact of CDM registration	Remarks
Rice husk based renewable energy generation through gasification for rice mills	AMS-I.B.	X	√ IB, TB, PPB	√	√	X	√	√	X	Other barrier including lack of information dissemination
Biomass gasification based power generation by Arashi Hi-Tech Bio-Power Pvt. Ltd.	AMS-I.D.	X	√ TB, PPB	√	X	X	√	√	X	Investment risk due to the escalation in the price of biomass.
Sri Gomathy Mills – 1.4 MW biomass gasification based power generation and waste heat recovery system for captive utilization	AMS-I.C.	X	√ IB, TB, PPB	√	X	X	√	√	√	Biomass pricing is dynamic in the region and seasonal fluctuations will lead to uncertainties in the process of biomass supply chain.

Title	Methodology	Investment Analysis	Barrier Analysis	Prevailing practice barrier	Identification of alternatives	Institutional /Regulatory Barriers	Technology Barriers	Common Practice Analysis	Impact of CDM registration	Remarks
100 village biomass gasifier based power plants totaling 5.15 MW for decentralized Energy Systems India Pvt. Ltd.	AMS-I.A.	X	√ IB, TB, PPB	√	√	X	√	X	X	Institutional barriers or limited information, managerial resources, financial resources, organizational capacity, or capacity to absorb new technologies.

IB: Investment barrier; PP: Prevailing practice barrier; TB: Technological barrier.

Source: cdm.unfccc.int and own estimates.

parameters affecting the power export and CO_2 emissions. For projects consuming biomass a specific fuel consumption of each type of fuel (biomass or fossil) to be used should be specified ex-ante. The consumption of each type of fuel shall be monitored.

5.4. Leakages

According to the general guidance of the Appendix B of the simplified modalities and procedures for small-scale CDM project activities biomass project's leakage shall be considered (see: para. 8) only within the boundaries of non-Annex-I Parties (see: para. 9). Leakage is defined as the net change of anthropogenic emissions by sources of GHG which occurs outside the project boundary, and which is measurable and attributable to the CDM project activity. It occurs when an emission reduction from the project directly or indirectly causes an emission increase at other location or time (Ghosh et al., 2002). Leakage due to diversion of fuel from other uses is likely here. Wood from forests, eucalyptus, and agricultural residues are normally used as fuel and raw material in the Indian context.

6. ESTIMATION OF CDM POTENTIAL OF BIOMASS GASIFICATION PROJECTS IN INDIA

The amount of CO_2 emissions saved by a biomass gasification project would essentially depend upon the amount(s) of fuel(s) saved by its use, which, in turn, depend upon the annual useful energy provided by the biomass gasifier based power project. In case of electricity substitution, the gross annual CO_2 emissions reduced by a biomass gasifier based power project, GCE_{bg}, can be estimated as

$$GCE_{bg} = \left(8760 \; CUF_{bg} \; P_{bg} \right) CEF_e \tag{4}$$

where P_{bg} (in MW) represents the capacity of biomass gasifier based power project, CUF_{bg} (in fraction) the capacity utilization factor of biomass gasifier based power project, CEF_e the CO_2 emission factor of electricity. The term inside the second bracket of the right hand side of Eq. (4) is the annual amount of electricity saved by a biomass gasifier based power project.

There are five regional grids within the country viz. Northern, Western, Southern, Eastern and North-Eastern and different states are connected to one of the five regional grids (CEA, 2006). The CO_2 emissions mitigation through biomass gasification projects in India is estimated on the bases of the regional baseline. With respect to CEFe the range of regional grid average emissions factors in India ranges from 420 gCO_2/kWh in the North-eastern grid to 1050 g CO_2/kWh in the Eastern grid as per the latest updated baseline carbon dioxide emissions from power sector (version 2) by the Central Electricity Authority (CEA) of the Government of India. Table 6 presents the CDM potential of biomass gasification projects in India on the basis of the regional baselines. The gross annual CER potential has been estimated at about 58 MT. Among all the states in India, Kerala has the largest annual CO_2 emissions mitigation potential through biomass gasification (i. e. 6.72 million tonne) followed by West Bengal (6.42 million tonne), Andhra Pradesh (6.40 million tonne), Karnataka (5.86

million tonne), Tamilnadu (5.85 million tonne), Uttar Pradesh (4.96 million tonne) and so on. Table 7 presents the crop residue-wise break-up of the CDM potential of biomass gasification. It is observed that among all the agricultural residues considered in this study rice husk has a huge potential of CO_2 emissions mitigation (17 million tonne) followed by coconut-coir 15 million tonne, maize stalks (11 million tonne) and mustard stalk (4 million tonne).

Figure 6 presents the results of a sensitivity analysis undertaken to study the effect of the capacity utilization factor of the biomass gasification system on the annual electricity generation and annual CER potential of biomass gasifier based power project in India.

Table 6. Annual gross CO_2 emissions mitigation potential of biomass gasification projects in India

State	Annual electricity generation (TWh)	CO_2 emissions mitigation potential (million tonn)		
		Region	Baseline* (kg CO_2/kWh)	Estimated potential (million CER)
Andhra Pradesh	7.45	Southern	0.86	6.40
Assam	1.49	North Eastern	0.42	0.63
Bihar	3.69	Eastern	1.05	3.86
Chhattisgarh	0.74	Western	0.81	0.60
Goa	0.17	Western	0.81	0.14
Gujarat	2.00	Western	0.81	1.62
Haryana	1.81	Northern	0.80	1.45
Himachal Pradesh	0.16	Northern	0.80	0.12
Jammu and Kashmir	0.69	Northern	0.80	0.55
Jharkhand	0.55	Eastern	1.05	0.57
Karnataka	6.82	Southern	0.86	5.86
Kerala	7.82	Southern	0.86	6.72
Madhya Pradesh	2.59	Western	0.81	2.10
Maharashtra	2.43	Western	0.81	1.97
Meghalaya	0.01	North Eastern	0.42	0.01
Orissa	1.34	Eastern	1.05	1.40
Punjab	3.21	Northern	0.80	2.56
Rajasthan	3.32	Northern	0.80	2.65
Tamil Nadu	6.80	Southern	0.86	5.85
Uttar Pradesh	6.22	Northern	0.80	4.96
West Bengal	6.13	Eastern	1.05	6.42
Others	1.81	---*	0.85	1.54
All India	67.25			57.98

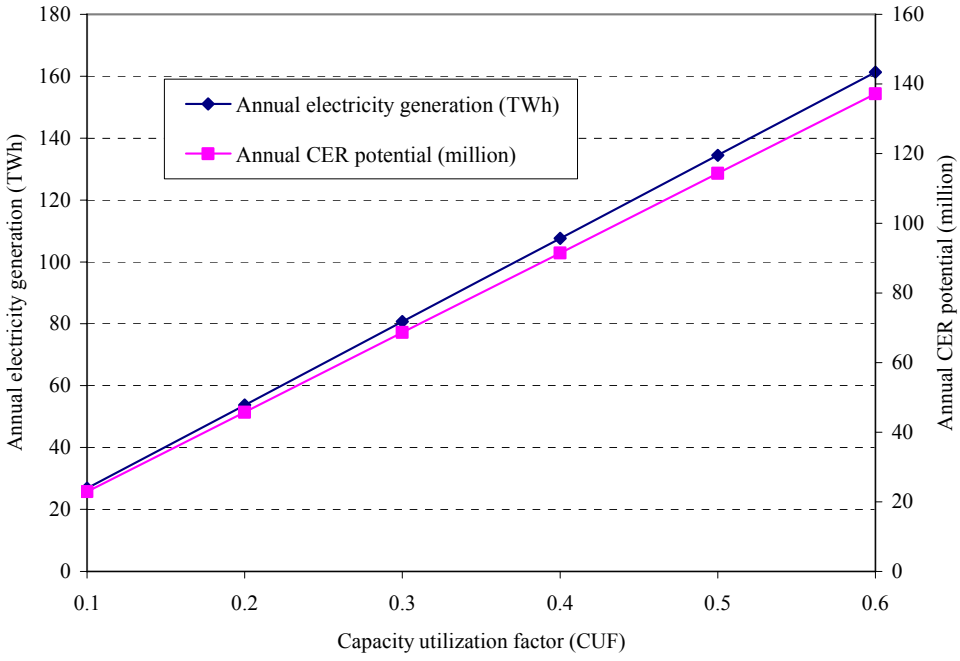
Source: http://www.cea.nic.in/planning/c%20and%20e/Government%20of%20India%20website.htm and own estimates.

*All India average emission factor 0.85 kg CO2/kWh has been used.

Table 7. Crop residue-wise break-up of the annual gross CO_2 emissions mitigation potential through biomass gasification projects in India

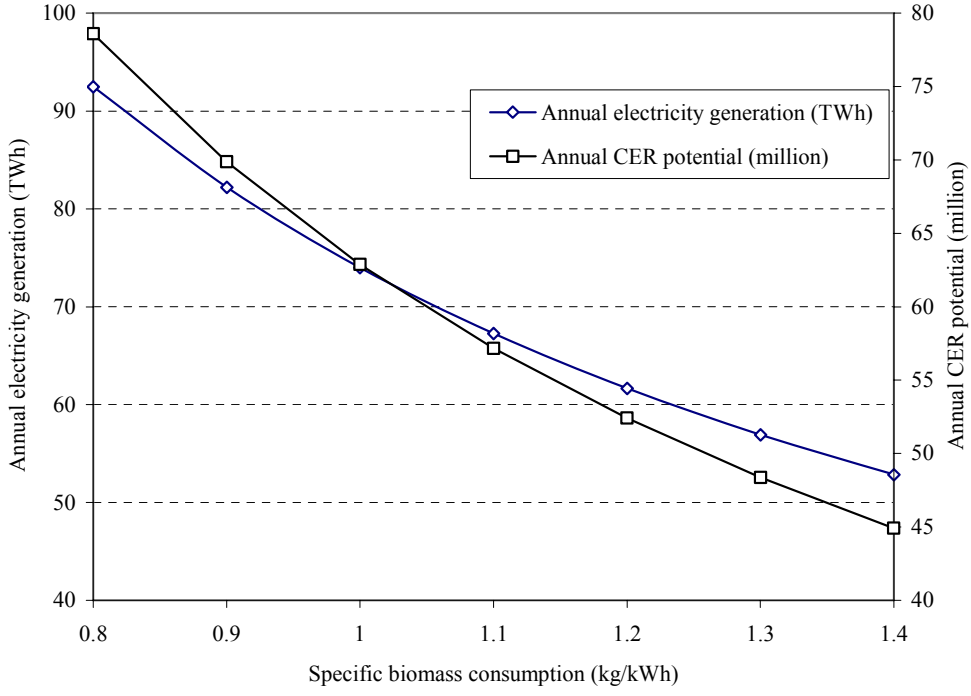
State	Annual gross CO_2 emissions mitigation potential (million CER): crop residue wise break-up								
	Rice husk	Maize cobs	Maize Stalks	Arhar stalk	Groundnut shells	Cotton stalk	Jute and Mesta sticks	Mustard stalk	Coconut coir
Andhra Pradesh	2.26	0.26	1.33	0.17	0.40	0.51	0.17	NA	1.31
Assam	0.39	NA	NA	NA	NA	NA	0.08	0.08	0.08
Bihar	1.30	0.32	1.66	0.06	NA	NA	0.39	0.13	NA
Chhattisgarh	0.60	NA	NA	NA	NA	NA	NA	NA	NA
Goa	NA	NA	NA	NA	NA	NA	NA	NA	0.14
Gujarat	0.19	0.10	0.55	0.08	0.13	0.33	NA	0.24	NA
Haryana	0.49	NA	NA	NA	NA	0.39	NA	0.56	NA
Himachal Pradesh	0.12	NA	NA	NA	NA	NA	NA	NA	NA
Jammu and Kashmir	NA	0.09	0.46	NA	NA	NA	NA	NA	NA
Jharkhand	0.39	0.02	0.12	0.03	NA	NA	NA	NA	NA
Karnataka	0.74	0.38	1.97	0.21	0.18	0.30	NA	NA	2.10
Kerala	0.15	NA	NA	NA	NA	NA	NA	NA	6.57
Madhya Pradesh	0.18	0.20	1.06	0.17	0.04	0.07	NA	0.38	NA
Maharashtra	0.36	0.04	0.19	0.49	0.09	0.52	0.01	NA	0.28
Meghalaya	NA	NA	NA	NA	NA	NA	0.01	NA	NA
Orissa	1.11	NA	NA	0.08	0.01	NA	0.04	NA	0.16
Punjab	1.67	0.08	0.40	NA	NA	0.34	NA	0.07	NA
Rajasthan	NA	0.17	0.87	NA	0.03	0.23	NA	1.34	NA
Tamil Nadu	1.42	0.03	0.18	0.05	0.29	0.10	NA	NA	3.77
Uttar Pradesh	2.11	0.25	1.29	0.37	0.02	NA	NA	0.92	NA
West Bengal	2.98	0.02	0.10	NA	NA	NA	2.26	0.57	0.48
Others	0.60	0.08	0.43	0.04	0.02	0.03	0.01	0.14	0.18
All India	17.08	2.04	10.61	1.74	1.21	2.81	2.98	4.44	15.06

Source: own estimates.



Source: Own estimates.

Figure 6. Effect of capacity utilization factor of the biomass gasifier based power project on the annual electricity generation and CER potential.



Source: Own estimates.

Figure 7. Effect of specific biomass consumption on the estimated potential of biomass power projects.

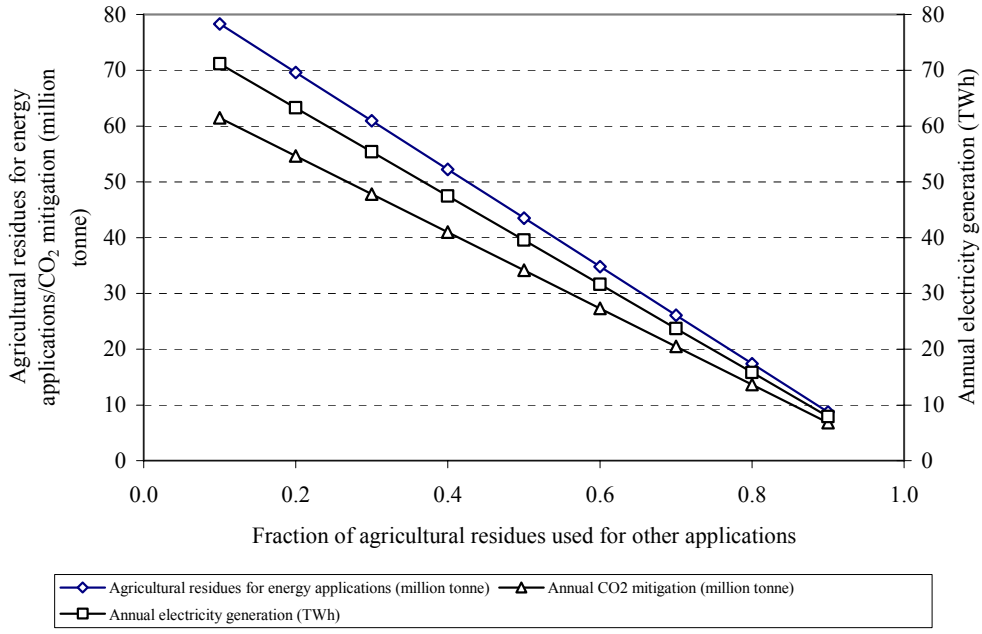


Figure 8. Effect of the fraction of agricultural residues used for other applications on the estimated potential of biomass power projects.

Similarly, the effect of specific biomass consumption on the annual electricity generation and annual CER potential is shown in Figure 7. It may be noted that the CDM potential of biomass gasification is highly sensitive to the values of the CUF_{bg} and specific biomass consumption. The macro level estimates for the CDM potential of biomass gasification projects obtained based on this study will further increase with technological improvements (i.e. reduction in specific biomass consumption and increase in the capacity utilization factor) of biomass gasifier based power projects. Figure 8 presents the effect of the fraction of agricultural residues used for other applications (see Eq. 2) on the estimated potential of biomass power projects. As expected, the annual electricity generation and associated CDM potential of biomass gasifier based power projects will decrease with increased use of agricultural residues for other applications.

7. PROSPECTS OF BIOMASS GASIFICATION PROJECTS IN INDIA

In the literature, studies on the process of diffusion of new technologies provide a useful framework to examine the acceptance of energy systems. “Communication and diffusion of innovation” theories suggest that the acceptance of innovations is influenced by the characteristics of the innovation and also the process by which the communication takes place in the community. The acceptance of an idea by an individual usually follows a process of awareness, knowledge and action. The information provided from different sources creates awareness and knowledge which may lead to adoption. The product characteristics are also indicated to affect the rate at which diffusion takes place. The relative advantage of the innovation over its substitutes is an important influence on its acceptance (Rogers, 1995).

Moreover, the propensity to adopt will depend on costs and benefits from adoption which typically differ among potential adopters due to differences with regard to size, organization, products, type of manufacturing process, economic life time of manufacturing processes, technology capabilities, management, relation with external parties and their financial situation (Kemp and Volpi, 2008).

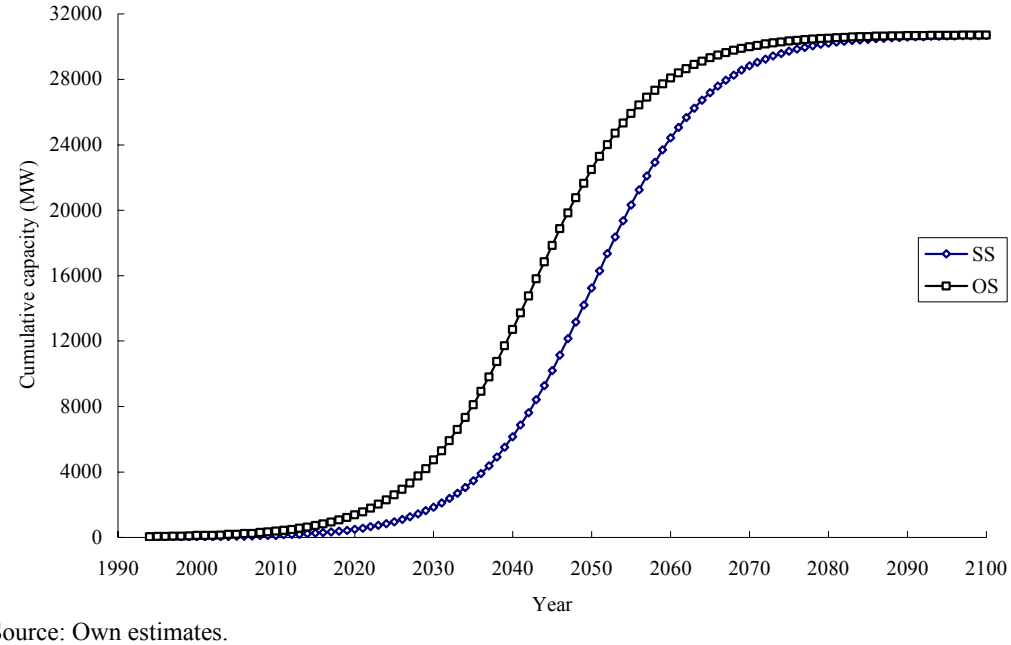
Islam and Haque (1994) observed that the diffusion of a technology measured in terms of the cumulative number of adopters usually conforms to an exponential curve as long as the new technologies manage to become competitive with incumbent technologies. Otherwise, the steep section of the curve would never be reached because technology use falls back to zero at the removal of subsidies (Purohit and Michaelowa, 2008a). The exponential growth pattern may be of three types – (i) simple exponential, (ii) modified exponential, and (iii) S-curve. Out of these three growth patterns, the simple exponential pattern is not applicable for the dissemination of renewable energy technologies, as it would imply infinite growth (Islam and Meade, 1997). The modified exponential pattern (with a finite upper limit) is more reasonable but such a curve may not match the growth pattern in the initial stage of diffusion (Martino, 2003). Empirical studies have shown that in a variety of situations the growth of a technology over time may conform to an S-shaped curve, which is a combination of simple and modified exponential curves. The S-shaped curves are characterized by a slow initial growth, followed by rapid growth after a certain take-off point and then again a slow growth towards a finite upper limit to the dissemination (Purohit, 2009). Therefore, in this study, a logistic model is used to estimate the theoretical cumulative capacity of biomass gasification projects at different time periods. The logistic model (or logistic growth curve) is continuous in time. The growth curve of a technology growing according to logistic growth is typically characterized by three phases: an initial *establishment* phase in which growth is slow, a rapid *expansion* phase in which the technology grows relatively quickly, and a long *entrenchment* stage in which the technology is close to its limiting potential due to intra-species competition.

As per the logistic model, the cumulative capacity, P(t), of the biomass gasification projects disseminated up to a particular period (t^{th} year) can be expressed as (Loulu et al., 1997; Purohit and Kandpal, 2005)

$$P(t) = P_{max}\left[\frac{e^{(a+bt)}}{1+e^{(a+bt)}}\right] \tag{5}$$

where P_{max} represents the estimated maximum utilization potential of the the biomass gasification projects in the country. The regression coefficients a and b are estimated by a linear regression of the log-log form of Eq. (5) as given below.

$$ln\left[\left(\frac{P(t)}{P_{max}}\right) \Big/ \left\{1-\left(\frac{P(t)}{P_{max}}\right)\right\}\right] = a + b\,t \tag{6}$$



Source: Own estimates.

Figure 9. Time variation of cumulative capacity of biomass gasification projects in India using Logistic model.

Figure 9 represents the projected time variation of the cumulative capacity of biomass gasification projects using the logistic model considered in the study. Two cases such as business as usual or standard scenario (SS) and optimistic scenario (OS) are presented. The values of the regression coefficients using a logistic model have been estimated by regression of the time series data for the installation of biomass gasification projects extracted from the annual reports of the MNRE. In the optimistic scenario it is assumed that, in the past, if the diffusion of biomass gasification projects would have been driven by the market forces instead of subsidies then the cumulative capacity of installation of biomass gasification projects would be three times more than the actual level (Purohit and Michaelowa, 2007, 2008b). The preliminary results indicate that in India, even with highly favourable assumptions, the dissemination of biomass gasification projects is not likely to reach its maximum estimated potential in another 50 years. But all these time periods are not relevant for the CDM whose current endpoint is 2012 and which may only be able to live longer if post-2012 negotiations retain an emission target based policy regime. However, CDM could be used as a tool to foster the dissemination of biomass gasification projects in the country. It could accelerate the diffusion process. Table 8 presents the projected values of the cumulative capacity of biomass power and likely CER generation using the logistic model while Figure 10 shows the development over time. It may be noted that with the current trend of dissemination of biomass gasification projects in the country around 166 MW capacity could be installed up to the end of first crediting period in the SS scenario whereas in the OS scenario 478 MW capacity could be installed. Up to the year 2020, more than 1300 MW capacity of the biomass gasification projects are expected to be installed that would generate 3 million CERs.

Table 8. Projected values of the cumulative capacity of biomass gasifier based projects and associated CER generation

Year	Projected values of the cumulative capacity (MW)		Projected values of the annual electricity generation (TWh)		Projected values of the annual CER generation (million CER)	
	SS	OS	SS	OS	SS	OS
2008	96	280	0.21	0.61	0.18	0.52
2012	166	478	0.36	1.05	0.31	0.89
2016	285	814	0.62	1.78	0.53	1.51
2020	490	1373	1.07	3.01	0.91	2.56

*Baseline 850g CO_2/kWh.
Source: own estimates.

CONCLUSIONS

A preliminary assessment of CDM potential of biomass gasification projects in India has been made in this study. The results indicate that, there is a vast theoretical potential of CO_2 emissions mitigation by the use of biomass gasification projects in India. On the basis of a simple framework developed for the estimation of effective potential availability of agricultural residues for energy applications in India it is observed that around 74 million tonne agricultural residues as a biomass feedstock can be used for energy applications on an annual basis. However, effective and efficient utilization of agricultural residues is critically important. On the basis of the theoretical estimates presented in this study the potential of biomass gasification projects could reach 31 GW in terms of plant capacity that can generate more than 67 TWh electricity annually. The preliminary estimates presented in this study indicate that annual CER potential of biomass gasification projects in India could theoretically reach 58 million tonnes. Under more realistic assumptions about diffusion of biomass power projects based on past experiences with the government-run programmes, annual CER volumes by 2012 could reach 0.4 to 1.0 million and 1.0 to 3.0 million by 2020. The projections based on the past diffusion trend indicate that in India, even with highly favorable assumptions, the dissemination of biomass gasification projects is not likely to reach its maximum estimated potential in another 50 years. CDM could help to achieve the maximum utilization potential more rapidly as compared to the current diffusion trend if supportive policies are introduced.

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Chapter 14

BIOMASS GASIFICATION IN CHINA: SOME RECENT RESEARCH AND DEMONSTRATION

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ABSTRACT

In china, considerable research has been carried out to develop advanced biomass technology in order to improve the biomass energy utilization efficiency. In this chapter, some recent research on biomass gasification technology is reviewed including down-draft gasifier, circulating fluidized-bed (cfb) gasifier, and biomass gasification for power generation (bgpg), and arc plasma gasifier. The project background, technology adopted, current status, process economics and existing problems of the following two demonstration projects are discussed in detail: (1) the integrated biomass gasification and gas-supply system demonstration project in shandong province: demonstration stations for biomass gasification and gas-supply were constructed in rural villages in this project. These stations processed agricultural residues such as straw into gas fuel using down-draft gasifiers. (2) the biomass gasification and power generation system demonstration project in hainan province: an mw-scale biomass power plant was constructed at the sanya timber factory. This biomass power plant adopted advanced cfb gasifier system, and made use of the wood waste generated in the sanya timber factory as fuel, and reached the electricity generation capacity up to 1.2mw.

1. INTRODUCTION

Biomass is often regarded as a storable, transportable and renewable energy source; it distributes widely in the environment and is available in numerous forms such as wood, grass, agricultural waste, and garbage. The characteristics of biomass fuel have certain similarity

with those of coal, so their processing and utilization techniques are similar. Through modern technologies biomass can be converted into gas, oil, and solid fuels. Another important advantage of biomass energy is that, from a carbon recycle viewpoint, it has zero co_2 emission; this may alleviate or even resolve the global warming problem caused by excessive consumption of fossil fuels. Thus in many countries biomass energy is considered as an important alternative energy source for the reasons: (a) controlling co_2 emission, (b) avoiding discharge of toxic substances harmful to human being and the nature, and (c) improving the ecological system by related measures such as planting energy crops.

In china, there is on one hand an enormous amount of biomass resources, mainly from the agricultural and forest sectors, and on the other hand there has been, for a long time, insufficient energy supply in rural areas [1, 2]. It has long been recognized that it has become urgent to develop advanced processes for conversion of biomass into clean and convenient fuels in the country, so as to raise the energy utilization efficiency and decrease domestic air pollution [3-5]. Several chinese institutes have studied various biomass energy conversion technologies and applied them in a number of demonstration projects in rural areas. The recent development in biomass gasification will be reviewed in this chapter.

2. BIOMASS RESOURCE IN CHINA

As an agricultural country, china has abundant biomass resources mainly in the form of agricultural and forest wastes. The amount of biomass waste generated per year is estimated to be close to 0.65 billion tons, and is predicted to reach 0.726 billion tons, equal to 0.5 billion tons of coal equivalent (tce), by 2010 [1, 6]. The quantity of straw and forest residues is very large; the quantity of forest residues alone (firewood forest excluded) reaches 37 million cubic meters per year, equal to 20 million tons of coal equivalent. Considering also the increasing amount of municipal solid waste, sewage sludge, livestock excrement and other biomass resources, the annual amount of biomass resource in china can be over 0.6 billion tons of coal equivalent. If taking a part of biomass out as feedstuff and other usages, the remaining biomass resource that can be used for energy purposes is about 0.3 billion tons of coal equivalent. With further development of agriculture and forest industry, especially with the exploitation and popularization of fast-grown firewood forest and energy crop, the biomass resource in china is likely to become even more significant in the future and have great exploitation and utilization potential.

It is very important to limit the environmental pollution caused by these biomass wastes, and make reasonable use of their energy content to provide energy supply to the rural areas.

Traditionally, biomass is a major energy source in china, especially in its rural areas. Crop and forest residues are two sources of biomass and mainly used as fuels for cooking food and warming house by way of direct burning in stoves. But the efficiency of heat utilization is very low in these traditional ways of biomass burning; and incomplete combustion had often caused serious pollution. So in the 1990s china has paid more attention on developing new and efficient technologies to convert biomass into convenient and clean energy products.

3. RESEARCH ON BIOMASS GASIFICATION

Biomass gasification is a technology that converts biomass material into gaseous fuel. Under different technology routes, a combustible gas of low- or medium-heating value can be produced [7, 8]. The main benefits of biomass gasification are that the utilization efficiency is increased after the biomass is converted into gaseous fuel, which has wider applications such as city gas, burning in utility boilers, gas turbines or gas engines to generate electricity. Its main demerits are that the conversion system is more complex, and the produced gas is not convenient to be stored and transported, so special matched utilization of the gas is required. A number of biomass gasification technology such as down-draft gasifier, circulating fluidized-bed (CFB) gasifier, biomass gasification for power generation (bgpg), and plasma gasifier have been studied extensively.

3.1. Down-Draft Gasifier

A model of down-draft gasifier tested by huang et al. [9, 10] is shown schematically in figure 1.

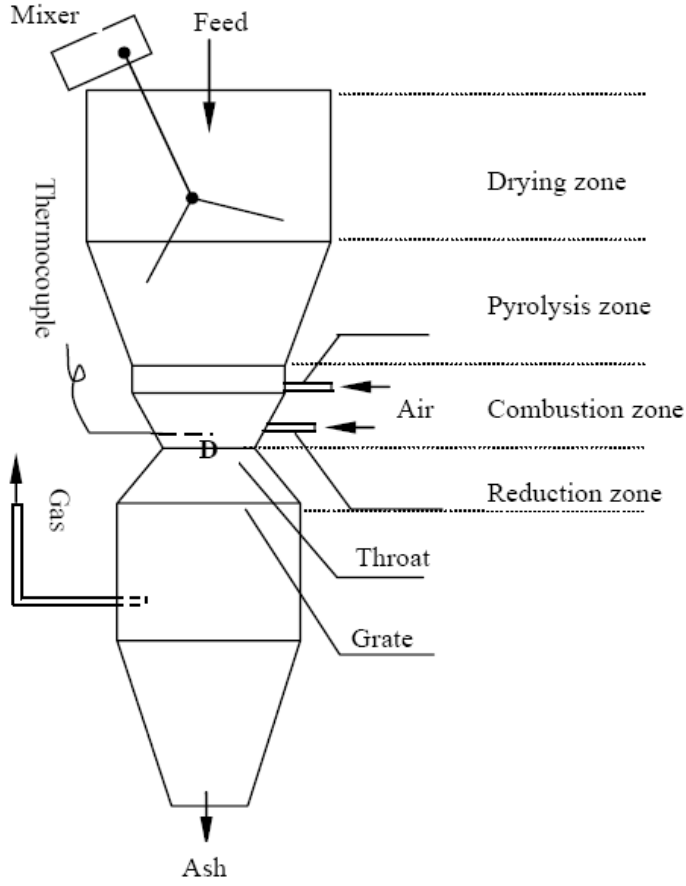

Figure 1. Schematic of a down-draft gasifier (ref. [9]).

Biomass is fed into the upper part of the gasifier, which has an internal diameter of 500mm. A throat section is located at the middle part of the gasifier (throat diameter d=180mm). Air is introduced into the gasifier above the throat section. A grate is installed beneath the throat section. The combustible gas is withdrawn from the lower part of the gasifier, whereas the ash is discharged from the bottom of the gasifier. The drying, pyrolysis, combustion and reduction reaction zones are roughly indicated in the figure.

Experimental data for gasification of wood, rice hull, and mixed garbage are given in table 1, 2 and 3, respectively. The main combustible gas components are h_2, co, ch_4, c_2h_4, c_2h_6, etc. The calorific value of the produced gas can reach 4.9mj/nm^3 for wood gasification, but is only about 3.8 mj/nm^3 for rice hull gasification.

Table 1. Experimental data of wood gasification in a down-draft gasifier

Gas sample No.	1	2
Run time(min)	15	35
Upper air flow rate (Nm^3/h)	9.8	10
Throat air flow rate (Nm^3/h)	18	14
Temperature of throat zone (^{0}C)	900	870
Gas composition (%)		
H_2	9.87	11.56
CH_4	2.03	1.99
CO	18.73	18.02
C_2H_4	1.03	0.49
C_2H_6	0.14	0.03
O_2	0.38	0.89
N_2	53.63	52.51
CO_2	13.45	14.5
Lower heating value of gas (kJ/Nm^3)	4900.6	4566.2

Table 2. Experimental data of rice hull gasification in a down-draft gasifier

Gas sample No.	1	2
Run time(min)	10	35
Upper air flow rate (Nm^3/h)	5	17
Throat air flow rate (Nm^3/h)	18	5
Temperature of throat zone (^{0}C)	1162	1234
Gas composition (%)		
H_2	5.26	6.39
CH_4	0.9	1.82
CO	20.85	17.45
C_2H_4	0	0.46
C_2H_6	0	0.02
O_2	0.21	0.56
N_2	58.7	59.2
CO_2	14.07	14.11
Lower heating value of gas (kJ/Nm^3)	3517.5	3854.8

Table 3. Experimental data of mixed garbage gasification in a down-draft gasifier

Gas sample No.	1	2	3	4	5
Run time (min)	8	10	18	22	34
Upper air flow rate (Nm^3/h)	13	13	13	13	18
Throat air flow rate (Nm^3/h)	20	20	20	20	25
Temperature of throat zone (^0C)	837	870	944	1085	1153
Gas composition (%)					
H_2	11.81	11.78	9.11	9.3	9.19
CH_4	2.29	1.48	1.02	0.94	0.74
CO	14.82	15.57	17.2	16.77	15.25
C_2H_4	0.85	0.37	0.06	0.02	0.02
C_2H_6	0.09	0.03	0	0	0
O_2	0.26	0.81	0.93	0.82	0.76
N_2	53.67	56.12	59.78	60.11	60.75
CO_2	12.86	10.93	11.9	12.06	10.95
Lower heating value of gas (kJ/Nm^3)	4561.2	3894.2	3554.5	3463.3	3175

3.2. Circulating Fluidized-Bed (CFB) Gasifier

A model of circulating fluidized-bed gasifier studied extensively by xu et al. [5, 11-13] is shown schematically in figure 2. Air is introduced into the bottom of the gasifier through an air distributor. Biomass powder is continuously fed into the lower part of the gasifier through an l-valve. The temperature of the gasifier is about 750-900^{0}C. Biomass powder is quickly fluidized inside the gasifier while undergoing pyrolysis and gasification reactions, and is converted into gas and char. The cyclone connected to the gasifier outlet pipe separates the char from the gas. Then the char is returned into the lower part of the gasifier through an l-valve, and is utilized in further gasification reactions.

Table 4 shows the main operating parameters of the circulating fluidized-bed gasifier.

Table 4. Main operating parameters of a circulating fluidized-bed gasifier

Reactor type	Circulating fluidized-bed
Height	8m
Diameter (internal)	1.8m
Feeding point height	1.7m
Air distributor	Perforated plate with openings for pipes
Construction material	Carbon steel
Insulation material	Refractory bricks
Insulation thickness	250mm
Equivalence ratio	0.2-0.25
Reaction temperature in the fluidized bed	750-900℃
Pressure	1atm
Biomass feed rate	900-1500kg/h
Flow of air in the reactor	1000-1600m^3/h
Mean particle size of biomass feed	0.22mm
Average gas residence time	21s

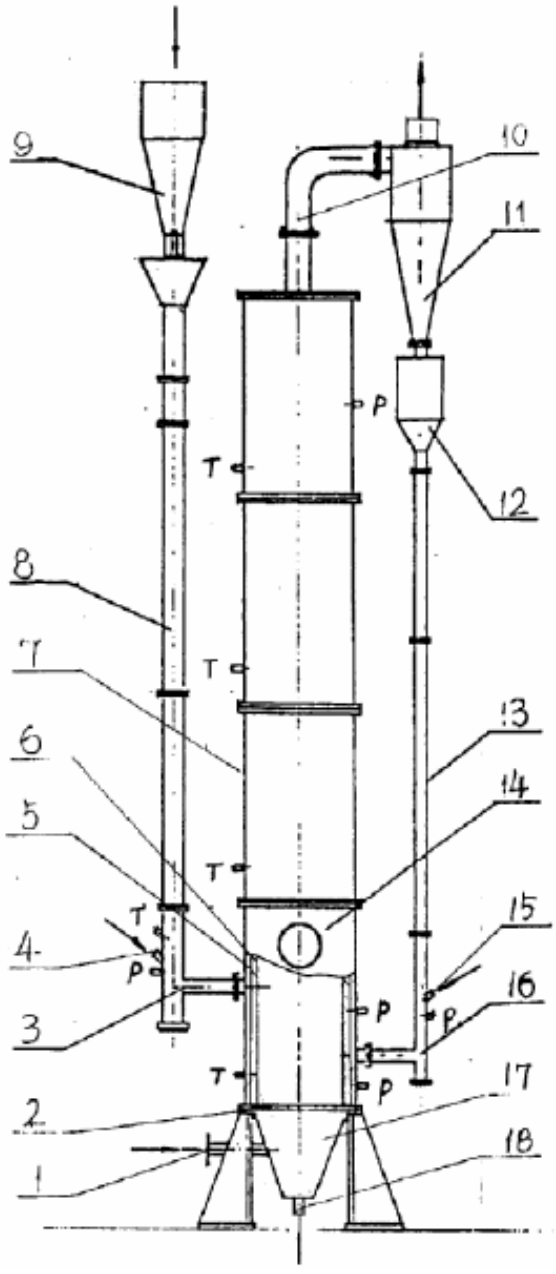

Figure 2. Schematic of a circulating fluidized-bed gasifier (ref. [11]). (1. Air inlet of gasifier. 2. Air distributor. 3. L-valve. 4. Air inlet of L-valve. 5. Heat insulation material. 6. Heat resistant material. 7. Steel wall. 8. Feed tube. 9. Feed hopper. 10. Gas outlet pipe. 11. Cyclone. 12. Char hopper. 13. Circulating pipe. 14. Fluidized bed. 15. Air inlet of L-valve. 16. L-valve for char circulation. 17. Wind box. 18. Ash discharge. T: Temperature measuring point. P: Pressure measuring point.)

And table 5 presents selected experimental data of wood gasification. The advantages of circulating fluidized-bed gasifiers are that they can achieve a higher carbon conversion efficiency and processing throughput. A number of biomass cfb gasifiers have been designed and constructed in china. In most cases the gas produced is used for direct boiler firing.

Table 5. Experimental data of a circulating fluidized-bed gasifier

Feed rate of wood (kg/h)	1500	885	885
Feed rate of air (Nm^3/h)	1650	1350	1610
Gasifier temperature (℃)	775	800	940
Gas composition (vol.%)			
H_2	7.59	6.33	7.04
CO	24.83	18.66	18.29
CO_2	13	11.57	13.76
CH_4	5.91	5.58	3.63
C_2H_6	0.3	0.11	0.6
C_2H_2	0.27	0.27	0.55
N_2	48	51.8	56
Lower heating value of gas (KJ/Nm^3)	6360	5300	5010

3.3. Biomass Gasification for Power Generation (BGPG)

Biomass gasification for power generation has been studied extensively aiming at the development of distributed power generating systems using agricultural and forest waste as fuel, which are suitable for application in rural areas. The conventional technologies already employed in china are rice hull gasification and power generation in rice mills, where the scale of the moving-bed gasifier used is small (the largest capacity is only 200 kw), which leads to lower economic benefit and some pollution problems. Recently, a biomass gasification and power generation system using circulating fluidized-bed gasifier has been built and tested by wu et al. [14-16]. The main parts of this bgpg system includes a biomass conveyer and feeder, a circulating fluidized-bed gasifier, a venturi purifying tube, a series of water scrubbers, a blower, six gas engine/generator sets, and a waste-water treatment pool. The flow diagram is shown in figure 3. Summary data of a bgpg system using cfb gasifier are given in table 6.

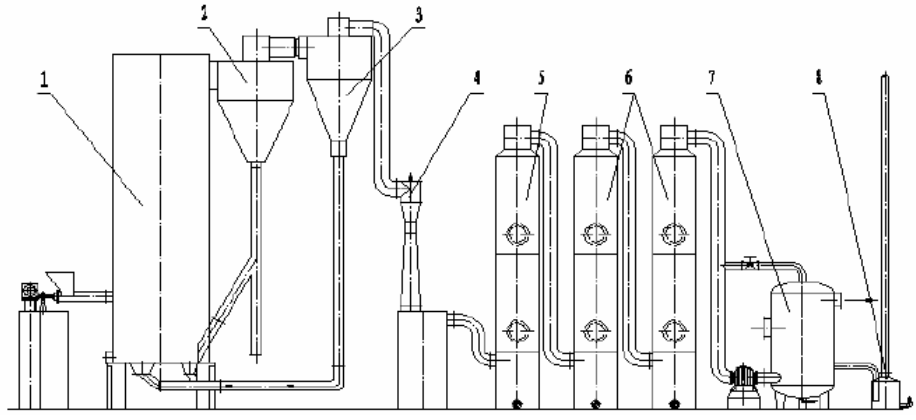

Figure 3. Flow diagram of biomass gasification and power generation plant (ref. [15]) (1. Gasifier. 2. Primary cyclone. 3. Secondary cyclone. 4. Venturi scrubber. 5. Water scrubber. 6. Water scrubber. 7. Gas tank. 8. Water seal).

Table 6. Summary data of a BGPG system based on CFB gasifier

Electrical capacity (kW)	1200kW
Gasifier type	Circulating fluidized-bed gasifier (CFBG)
Fuel type	Wood waste
Internal diameter of gasifier (m)	1.8
Feed rate of wood (kg/h)	800-1500
Gasifier temperature (^{0}C)	650-950
	4600-6300
Heating value of gas (kJ/Nm^3)	1.2-1.9
Fuel consumption (kg/kWh)	67-75
Cold gas efficiency (%)	Venturi scrubber (1 set) and tower scrubber (2 sets)
Gas cleaner	20
Water consumption (m^3/h)	200kW Hongyan gas engine/generator unit (6 sets)
Gas engine/generator	17
Thermal to electrical conversion efficiency (%)	3060
Capital cost (Yuan RMB/kW)	0.27
Electricity cost (Yuan RMB/kW)	

Currency exchange rate: 1 USD = 7.2 Yuan RMB.

Due to the relatively high gas velocity in cfb gasifiers, raw gases from biomass cfb gasifiers usually contain a considerable amount of ash and tar, which must be removed to avoid contamination, corrosion/erosion, and other operational problems in the gas engines. So, water scrubbing of the raw gases and waste-water treatment for partial re-circulation are adopted for gas cleaning. The cleaned gases are then stored in a gas tank, which provides a continuous fuel supply to drive the gas engine and power generation units.

3.4. Arc Plasma Gasifier

An arc plasma gasifier was tested by zhao et al. For treatment of biomass wastes [17, 18]. The arc plasma generator was located at the upper part of the reactor apparatus and had a rod-shaped tungsten cathode and a tube-shaped water-cooled copper anode; and argon and hydrogen gas mixture was used as working gas of the arc plasma generator. Direct current power from an electrical rectifier with an open-circuit voltage 540v was supplied to the two electrodes and produced arc discharges, so an argon/hydrogen plasma jet was generated. The biomass injector was located below the arc plasma generator; biomass powders from a screw feeder were injected using carrier gas (argon) into the plasma jet zone. The biomass feeding rate can be regulated by adjusting the speed of the screw feeder. The reacting plasma jet/biomass mixture then entered an extended reaction zone (inside diameter 30 mm, length 620 mm) made of 1cr18ni9ti steel with internal graphite lining. Typical operating conditions of the plasma apparatus is given in table 7.

Table 8 presents summary data of gaseous products from biomass pyrolysis in the dc arc plasma apparatus. The major components in gaseous product have been found to be h_2, co, c_2h_2 and ch_4.

Table 7. Operating conditions of the plasma apparatus

Arc Plasma Generator	
Voltage	270V
Current	150A
Power	40.5 kW
Working gas flow rate	3.2 m^3/h (H_2: 1.2 m^3/h + Ar: 2 m^3/h)
Biomass Powder Injector	
Carrier gas (Ar) flow rate	2 m^3/h
Biomass powder feed rate	1-4 g/s

A maximum carbon conversion of 79% and a maximum oxygen conversion of 72% from the biomass feed to gaseous products have been obtained under these experimental conditions. After pyrolysis experiments, inspection of the plasma reactor surface revealed that it was nearly free of residue, so that almost no tar was produced in plasma pyrolysis of biomass. The low tar level from plasma pyrolysis should be a significant advantage over other conventional pyrolysis methods. The product gas from plasma pyrolysis may be suitable for syngas applications such as methanol synthesis or ore reduction in iron and steel making industry. It may also be usable in fuel cells after the gas is further cleaned and processed. The specific power consumption in this experimental plasma apparatus under optimum conditions was estimated to be 3.7 kw·h/nm^3 (h_2 + co).

4. CHINESE DEMONSTRATION PROJECTS

In recent years, a number of demonstration projects concerning biomass gasification have been started up in various locations in china. Selected projects are reviewed in this section.

4.1. Integrated Biomass Gasification and Gas-Supply System (Shandong Province)

4.1.1. Background

The shandong province has active agricultural activities leading to a large surplus of agricultural residues, especially straw. Only a fraction of these biomass residues is utilized as energy source by farmers. Open burning in the field is a way widely practiced by farmers to dispose of most biomass residues. Such practice not only wastes the biomass, but also causes severe air pollution. Therefore, the government has sponsored a number of demonstration projects for integrated biomass gasification and gas-supply system. The objective of these projects is to convert straw into gas fuel by modern gasification technology and distribute the gas to household consumption. The projects in the shandong province were carried out mainly by the shandong institute of energy resources.

Table 8. Gaseous products from biomass pyrolysis in the plasma apparatus (the H2 value listed is net H2 production in the plasma apparatus; wt% is based on the amount of biomass feed)

Sample	Feeding Rate g/s	H_2		CH_4		C_2H_2		C^{2+}		CO		CO_2		Carbon Conversion (%)	Oxygen Conversion (%)
		Nm^3/h	wt%	Nm^3/h	wt%	Nm^3/h	wt%	Nm^3/h	wt%	Nm^3/h	wt%	Nm^3/h	wt%		
Wood A	2.56	4.71	4.56	0.12	0.93	0.22	2.77	0.04	0.56	1.99	26.99	0.06	1.28	35.4	35.91
(20-40mesh)	2.09	1.99	2.36	0.05	0.47	0.11	1.7	0.02	0.34	0.94	15.62	0.02	0.52	20.5	20.63
	1.75	2.88	4.08	0.05	0.57	0.18	3.32	0.02	0.41	1.26	25	0.07	2.18	34.3	35.32
Wood A	3.54	5.58	3.91	0.36	2.02	0.57	5.19	0.13	1.32	3.23	31.68	0.15	2.31	48.74	43.79
(40-80mesh)	3.06	5.51	4.47	0.34	2.2	0.51	5.37	0.12	1.41	3.32	37.67	0.15	2.67	55.56	51.87
	2.66	4.43	4.13	0.22	1.64	0.43	5.21	0.08	1.08	2.56	33.42	0.11	2.26	49.3	45.63
	2.53	4.28	4.2	0.25	1.96	0.42	5.35	0.09	1.28	2.56	35.13	0.11	2.37	52.22	47.89
	2.5	5.92	5.87	0.25	1.98	0.43	5.54	0.09	1.29	2.95	40.97	0.12	2.62	58.3	55.68
	2.22	6.27	7	0.3	2.68	0.59	8.57	0.1	1.62	3.41	53.33	0.12	2.95	78.98	72.04
Wood A	3.71	2.04	1.36	0.13	0.7	0.16	1.39	0.05	0.48	1.12	10.48	0.64	9.41	15.6	14.62
(<80mesh)	2.13	4.08	5.92	0.3	2.79	0.56	8.48	0.1	1.69	3.06	49.88	0.79	20.24	75.55	67.67
Wood B (40-80mesh)	2.5	3.28	3.25	0.17	1.35	0.28	3.61	0.07	1.01	1.88	26.11	0.06	1.31	36.94	33.68
Wood B (<80mesh)	3.28	2.04	1.54	0.2	1.21	0.3	2.95	0.08	0.88	1.75	18.52	0.08	1.33	27.95	24.48
Rice husk	1.78	5.01	6.98	0.14	1.56	0.16	2.9	0.04	0.81	1.49	29.06	0.07	2.15	39.16	37.59
(20-40mesh)	1.03	4.89	11.7	0.09	1.73	0.11	3.44	0.03	1.05	1.11	37.42	0.04	2.12	47.91	47.06
Rice husk	0.62	3.68	14.72	0.05	1.6	0.06	3.12	0.01	0.58	0.59	33.04	0.03	2.64	43.34	42.86
(40-80mesh)	2.5	1.94	1.92	0.11	0.87	0.12	1.55	0.04	0.58	1.19	16.53	0.06	1.31	21.98	21.43

4.1.2. Technology

Down-draft type gasifier suitable for straw gasification was adopted in the demonstration plants. The down-draft gasifier can reach gasification efficiency of 70-75%, the heating value of the producer gas is about 5 mj/nm^3, and the content of tar and dust in the producer gas after purification is less than 10 mg/nm^3. Straw is collected from the field, and dried under ambient condition till the moisture content is lower than 20%. Then using hay cutter, the straw is cut into a size of about 15-20 mm length. When fed into the gasifier, the straw undergoes pyrolysis, oxidation and reduction reactions, and is converted to combustible gas. The gas then passes purification system to remove dust and tar, and is pressurized and stored in gas tank. When needed, the gas is distributed to household users through a dedicated pipeline system.

4.1.3. Project Status

Due to the work of the shandong institute of energy resources, a number of demonstration plants for integrated biomass gasification and gas-supply have been constructed in the shandong province in recent years. The size of the rural villages having such gas-supply stations ranges from as small as having only 60 households, to as large as having more than 1000 households. A series of plant designs for various production capacities have been developed including gasifier, gas purification system, gas storage and distribution network. Provincial standard for construction of integrated biomass gasification and gas-supply stations has been established in the shandong province in order to guide commercialization and popularization of the technology.

4.1.4. Economics

The investments required for different sizes of integrated biomass gasification and gas-supply systems are listed in table 9. The cost of gas from such biomass gasification plants is less than 0.15 yuan rmb/nm^3, and decreases as the scale of the gasification plant increases. It has been estimated that for project of integrated biomass gasification and gas-supply systems, the project internal return rate is about 12%, and project investment recovery period is 8-9 years.

Table 9. Investment of integrated biomass gasification and gas-supply system

Number of household to be supplied	100	200	300	400	500
Total investment (thousand Yuan RMB)	204	284	364	414	464
Investment shared by each household (Yuan RMB)	2040	1420	1213	1055	928
Gas heating value (MJ/Nm^3)	5	5	5	5	5
Cost of gas (Yuan RMB/Nm^3)	0.15	0.12	0.103	0.091	0.084
Cost of gas (Yuan RMB/MJ)	0.03	0.024	0.0206	0.0182	0.0168

4.1.5. Problems

Some problems with the existing integrated biomass gasification and gas-supply systems are as follows:

(1) The heating value of the producer gas is relatively low, so during the peak hours a large volume of gas is required to satisfy all household need. This in turn demands a large gas storage and distribution capacity. Consequently, capital investment and construction cost are increased, and economic benefits of the projects are limited.
(2) Some small-scale gasification plants are in lack of automatic operation and control; and systems efficiency is too low.
(3) The producer gas contains a relatively high amount of tar; sometimes insufficient cleaning of the gas will contaminate the distribution network and cause troubles to the end-users.

4.2. Mw-Scale Biomass Gasification and Power Generation System (Hainan Province)

4.2.1. Background

Sanya timber factory is a large-scale timber processing enterprise located at sanya city of hainan province. In this factory there are two product lines imported from sweden for 30,000m^3 shaving plank and 40,000m^3 mid-density fiberboard production as well as other workshops. About 100 tons of wood waste is produced every day, which includes 35 tons wood powder, 10 tons leftover material, 10 tons sieving waste and 45 tons all kinds of bark. Due to the complicated sorts of timber waste, only some of the wastes are reused in the timber plant; most are disposed of by landfilling which causes severe problems of storage and pollution.

On the other hand, timber processing is a high electricity consumption activity; sanya timber factory needs power about 5000 kw and the electricity cost is up to ten million yuan rmb per year. So to convert the energy content of wood waste into electricity for the factory's self-consumption through biomass gasification and power generation technology has favorable benefits of environmental protection and energy conservation. Therefore, a project to build an mw-scale biomass gasification and power generation plant at the sanya timber factory was initiated by guangzhou institute of energy conversion.

4.2.2. Technology

The biomass gasification and power generation plant at sanya timber factory is composed of a circulating fluidized-bed (CFB) gasifier, gas-purifying systems, gas storage tank, gas engine/generator sets, waste-water treatment facility, fuel storage and feeding line, etc. During operation, biomass fuel is fed to the cbf gasifier through belt conveyer and screw feed, and undergoes thermal gasification reactions in the temperature range 650-950. The gas produced is de-dusted in cyclone separators, and further cleaned in a venturi scrubber and tower scrubbers by water spraying. The cleaned gas stored in a gas tank is used to drive any combination of six gas engine/generator sets to produce an electric power output ranging from 200 to 1200kw according to load demand. The electric power output is consumed by the sanya timber factory itself.

In this project, six sets of hongyan gas engine/generator units (each 200kw) are used for power generation. In china, the development work on gas engines is rather limited. The devices below 100kw are usually modified from diesel engines, and there is no approved product. Some development work has been done on gas engines over 500kw, but there are no

commercial models yet. As far as the commercial products are concerned, there are only two kinds of gas engines: 160kw and 200kw. Due to the small capacity of a single gas engine, the mw-scale biomass gasification and power generation plant at the sanya timber factory had to employ six gas engines together to reach the specified power capacity of 1200kw.

4.2.3. Project Status

Construction of the sanya biomass gasification and power generation plant began in early 1999, and was completed by the end of 1999. The plant was successfully started up in early 2000. During the test period, the cfb gasifier and gas cleaning system can be operated normally; and the gas engine/generator system is operated at about 60% of the rated load, providing a part of the power demand of the sanya timber factory. After extensive trial runs, in 2001 the plant entered its normal full operation phase, and was capable of providing power supply continuously to the sanya timber factory, making use of only waste wood from this factory as fuel. The following systems specifications have been obtained:

(1) The total designed capacity is 1200 kw; the average load for long-term operation is 85% of the designed capacity.
(2) The system failure rate is less than 10%; the maintenance shutdown rate is less than 10%.
(3) The total utilization rate is about 70%.
(4) The consumption of wood feed material is about 1.2 kg/kwh (dry); it is typically 30 tons each day.

4.2.4 Economics

4.2.4.1. Investment

The total investment for the sanya biomass gasification and power generation plant is 5.9 million yuan rmb including factory construction, equipment and other relevant costs; the detailed budget is shown in table 10.

4.2.4.2. Operation Cost

The operation cost of the biomass gasification and power generation plant includes:

(1) Feed material cost: this part of cost includes the feed material purchase, collection and transport. Due to that the feed material is provided by the sanya timber factory as waste material, the cost of feed material is about 0.06 yuan rmb/kwh.
(2) Workers' wages: this part of cost includes the wages for the administrators, operation workers of the biomass power plant and other laborers.
(3) Equipment maintenance expense: this part of cost includes the purchase of spare parts and damageable material, and maintenance fee.
(4) Plant administration expense: this part of cost includes the running expenses for daily official business of the biomass power plant.

The detailed analysis of operation cost of the biomass gasification and power generation station at sanya timber factory is given in table 11.

Table 10. Investment for the 1200kW biomass gasification and power generation plant at Sanya City of Hainan Province

Item	Quantity	Sum (10^4 Yuan RMB)
1. Building of workshops		70
1) Main workshop	300 m^2	25
2) Civil work	300 m^2	10
3) Foundation		10
4) Waste-water pool	300 m^3	10
5) Biomass storage field	600 m^2	15
2. Equipment manufacture		350
1) Gas engine	6 sets	165
2) CFB Gasifier	1 set	55
3) Purifying system	1 set	20
4) Waste-water treatment	1 set	35
5) Water cooling tower	2 sets	5
6) Conveyer	1 set	5
7) Electricity distribution board	1 set	15
8) Electric appliance and cable		50
3. Equipment installation		20
1) Gasification system		5
2) Gas engine		10
3) Power board and distribution		5
4. Technology and regulation		100
1) Gasification regulation		5
2) Generator regulation		10
3) Power distribution regulation		5
4) Patent cost		80
5. Management cost		50
Total		590

Table 11. Operation cost of the 1200kW biomass gasification and power generation plant at Sanya City of Hainan Province

Item	Unit price	Sum (10^4 Yuan RMB/year)
1. Workers' wages		37.2
1) Administrator	20000Y/year	6.0
2) Operation workers	12000Y/year	25.2
3) Other labors	10000Y/year	6.0
2. Maintenance cost		28.5
1) Gasifier maintenance	500Y/day	2.0
2) Generator maintenance	500Y/day	1.5
3) Generator fittings		10.0
4) Lubricating oils		5.0
5) Others		10.0
3.Administration cost		10.8
1) Official business expenses	6000Y/month	7.2
2) Reception fee	3000Y/month	3.6
4. Raw material cost		40.0
Total		116.5

4.2.4.3. Output and Gross Profit

Mainly due to the power load characteristics of the sanya timber factory, the biomass power plant is required to operate continuously except the overhaul of production line of the sanya timber factory once a year. So the designed power output is up to 6.65 million kwh/year. The local electricity price at sanya city is 0.55 yuan rmb/kwh, so according to the analysis shown in table 12 the production value of the biomass power plant is about 3.48 million yuan rmb/year and the gross profit is 2.32 million yuan rmb/year.

Table 12. Profit forecasting of the 1200kW biomass gasification and power generation plant at Sanya City of Hainan Province

Item	Unit	Quantity	Method of calculation
1. Operation days	Days/year	330	
2. Operation time	Hours/day	24	
3. Self-consumption load	kW	40.0	
4. Power output	10^4kWh/year	665.3	24×330×1200×0.7
5. Self-consumption power	10^4 kWh/year	31.6	24×330×40
6. Power on sale	10^4 kWh/year	633.7	
7. Electricity price	Y/kWh	0.55	
8. Production value	10^4Y/year	348.5	633.7×0.55
9. Gross profit	10^4 Y/year	232.0	348.5-116.5

4.2.5. Problems

4.2.5.1. Improvement of Systems Efficiency

According to the test on the biomass gasification and power generation station at sanya timber factory, the overall conversion efficiency from the total heat value of wood fed to the gasifier to the total electrical power output of the station is about 17%, which is lower than the conversion efficiency of other types of power generation systems (for example, large-scale coal power station is about 25%, Integrated Gasification Combined Cycle (IGCC) plants can reach up to 45%). Such low efficiency of the biomass power station at sanya city is mainly limited by the gasification and gas engine efficiency; it is very difficult with small gas engines and power generators to attain an efficiency higher than 20%. Consequently, the biomass consumption is usually higher than 1.1 kg(dry)/kwh, so the process economics is decreased considerably due to this factor. In the long term, improvement of the systems efficiency through modification of the current gasification and generation technology and adopting advanced systems like igcc cycle is very important.

4.2.5.2. Waste-Water Treatment

The current way of gas cleaning by water scrubbing not only decreases the system efficiency, but also produces tar-containing waste-water. Because the problems caused by tar have not yet been well settled, it is necessary to invest on waste-water treatment facilities in order to avoid secondary pollution. The waste-water treatment facilities need rather large investment and space, and significantly limit the economic attraction of biomass gasification technology. So gas cleaning is the weakest section for biomass gasification systems; it should become a major study topic in future research work.

4.2.6 .Environmental and Social Benefits

When the demonstration plant operates under designed conditions, about 10 thousands tons of biomass wastes will be utilized every year, so the adverse environmental and social effects caused by landfilling are alleviated. At the same time, with the advantage of no net co_2 release from biomass power generation, more than 10 thousand tons of co_2 emissions can be avoided. Furthermore, compared with coal burning, biomass gasification and power generation leads to no or very little no_x and so_x emissions. In the long term, the environmental and social benefit of biomass energy technology should be significant.

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