

THERMOCHEMICAL CONVERSION OF BIOMASS

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Summary

Thermochemical biomass conversion does include a number of possible routes to produce from the initial biomass feedstock useful fuels and chemicals. The base of thermochemical conversion is the pyrolysis process, which includes all chemical changes occurring when heat is applied to a material in the absence of oxygen. The products of biomass pyrolysis include water, charcoal (or more correctly a carbonaceous solid), oils or tars, and permanent gases including methane, hydrogen, carbon monoxide, and carbon dioxide. The process can be carried out as slow or fast pyrolysis. The progression of traditional slow pyrolysis of a hardwood in a retort that collects the liquids and gases from the process is the following. Starting with 100% solid material at ambient temperature, by 250°C the solid mass is at 88%, less than 10% liquid, and only a few percent gas. Between 300°C and 350°C the char mass rapidly decreases to less than 60%, the liquids are 20% to 30%, and the gases are between 15% and 25%. The char at this stage contains some amount of both oxygen and hydrogen. Further heating of the char to 750°C will decrease the mass of the char, and while its composition moves closer to pure carbon, the yield of gas increases and that of liquids decreases. Typically the slow pyrolysis is conducted for hours to a maximum temperature of 400°C - 500°C. The charcoal yield is 35% to 40% by weight. The goal of fast pyrolysis is to produce liquid fuel from lignocellulosic biomass that can substitute for fuel oil in any application. The liquid can also be used to produce a range of specialty and commodity chemicals. The essential features of a fast pyrolysis process are very high heating and heat transfer rates, which often require a finely ground biomass feed. The main product of fast pyrolysis is bio-oil, which is obtained in yields of up to 80 wt% of dry feed. An extension of pyrolysis is the gasification – a thermal process, which is optimized to give the highest yield of carbon and energy in the gas phase. In most cases the gasification is carried out as a partial oxidation process, in which some air or oxygen is introduced to burn

part of the input biomass to provide the heat for pyrolysis and gasification. When oxidant is air, the product contains about 50% nitrogen. As a result the gas heating value of the fuel gas ranges from 4 - 6 MJ Nm⁻³. If pure oxygen is used gasification will produce medium calorific value (MCV) gases in the range of 10 - 20 MJ Nm⁻³. Different kinds of gasifiers are used to process the biomass. They differ by arrangement of the feedstock and air flow: the counter flow moving bed gasifier, fluidized bed gasifier, entrained flow gasifier, co-current moving bed gasifier. There are also gasifiers where the necessary heat is introduced from an external source (indirect gasifiers). In the last case a MCV gas can be produced.

Biomass as a feedstock has a number of qualities, which make its pyrolysis and gasification attractive for various applications. This Article describes the state of the art, the use and draw-backs of those processes.

1. Introduction

Pyrolysis is the fundamental chemical reaction process that is the precursor of both the gasification and combustion of solid fuels, and is simply defined as the chemical changes occurring when heat is applied to a material in the absence of oxygen. The products of biomass pyrolysis include water, charcoal (or more correctly a carbonaceous solid), oils or tars, and permanent gases including methane, hydrogen, carbon monoxide, and carbon dioxide. The nature of the changes in pyrolysis depend on the material being pyrolyzed, the final temperature of the pyrolysis process and the rate at which it is heated up. As typical lignocellulosic biomass materials such as wood, straws, and stalks are poor heat conductors, management of the rate of heating requires that the size of the particles being heated be quite small. Otherwise, in massive materials such as logs, the heating rate is very slow, and this determines the yield of pyrolysis products. Depending on the thermal environment and the final temperature, pyrolysis will yield mainly char at low temperatures, less than 450°C, when the heating rate is quite slow, and mainly gases at high temperatures, greater than 800°C, with rapid heating rates. At an intermediate temperature and under relatively high heating rates, the main product is a liquid bio-oil, a relatively recent discovery, which is just being turned to commercial applications. However, the bulk of commercial and technical pyrolysis processes are applied to the production of charcoal from biomass - a solid biofuel, which is then used as a reducing agent in metallurgy, as activated charcoal in absorption applications after chemical processing, and in domestic cooking in urban areas of the developing world.

Gasification is a complex thermal process that depends on the pyrolysis mechanism to generate gaseous precursors, which in the presence of reactive gases such as oxygen and steam convert the majority of the biomass into a fuel gas. The fuel gas product can in turn be further purified to syngas, which is mainly composed of carbon monoxide and hydrogen, and used to produce chemicals and liquid fuels over catalysts. The majority of fuel gas is used directly to fire processes such as kilns, as fuel in steam boilers, and increasingly as a gaseous fuel in internal combustion engines (ICEs) and gas turbines.

2. Pyrolysis Fundamentals

The pyrolysis process consumes energy and, in chemists terms, is described as an endothermic reaction. It is, however, only mildly endothermic; and a factor of much more

importance, in terms of energy demand in pyrolysis, is the water content of the starting biomass. The heat of vaporization of pure water is 2.26 kJ g^{-1} at 100°C , while the chemical energy content of wood is only about 18.6 kJ g^{-1} . If there is a high moisture content to begin with, the net energy yield of the pyrolysis process will be very low because the energy necessary for the pyrolysis and gasification processes comes mainly from combustion of one or more of the products of pyrolysis (e.g., char, oil/tar, or combustible gases). Since most biomass is hygroscopic, the removal of water is even more endothermic because of the energy required to overcome the absorption energy. The behavior of solid biomass during heating is a complex interaction between the removal of water and the pyrolysis process. This is further compounded by the occurrence of reactions between the pyrolysis products and the char (see section 4.2.4).

2.1. The Chemical Nature of Pyrolysis in the Solid and Gaseous States

Biomass is an organic material that is composed of polymers that have extensive chains of carbon atoms linked into macro-molecules. The polymer backbone chains consist of chemical bonds linking carbon with carbon, or carbon with oxygen, or sometimes other elements such as nitrogen or sulfur. Instead of describing polymers in terms of the atomic structure of the chain, most can be viewed as assemblies of some larger molecular unit. In the case of cellulose, that unit is the glucan moiety [essentially a molecule of glucose with one molecule of water missing ($\text{C}_6\text{H}_{10}\text{O}_5$)]. For hemicellulose, the unit is often a 5-carbon sugar, called xylose. However, hemicellulose polymers are not linear chains as in the cellulose polymer. Some are branched and other monomer units have side chains, with acetyl groups being very common. The lignin polymers are composed of phenyl propane subunits linked at various points on the monomer through C-C and C-O bonds. In addition, there are often side chain materials such as methoxy groups. As heat is applied, the chemical bonds become thermally activated and eventually some bonds break. In cellulose the bonds are broken at random locations along the chain composed of thousands of glucan moieties. The average number of glucan subunits in a chain is described as the degree of polymerization (Dp). Thus, as heat continues to be applied, the polymer goes from a small number of large polymer molecules with a very high Dp, towards many smaller polymers with lower Dp values. As the value of Dp falls to less than 10 or so, the term, polymer, is replaced by the word, oligomer. Depending on the temperature and the applied pressure, eventually the oligomers ranging from $\text{Dp} = 8 \rightarrow 1$ are volatile (at typical pyrolysis temperatures between 400°C and 600°C) and evaporate from the solid mass. These small fragments are all anhydro sugars; when $\text{Dp} = 2$, it is called cellobiosan, and the monomeric version with $\text{Dp} = 1$ is called levoglucosan. If these volatile anhydro sugars are not quickly removed from the high temperatures of the pyrolysis, they will also undergo thermal fragmentation, producing highly reactive small intermediates. These in turn, if not removed from the original solid material (as in vacuum pyrolysis), will undergo chemical reactions with the remaining solid materials and may result in the creation of new polymers or accelerate the breakdown of the original chains. These reactions, unlike the endothermic chain-breaking reactions, can release heat (i.e., are exothermic), and in the pyrolysis of massive materials can result in the propagation of a thermal wave that accelerates the overall pyrolysis reaction. The removal of the products of pyrolysis and quenching them by sweeping them from the pyrolysis reactor into a cold zone (often a condenser), results in their capture for use as chemicals or fuels. Hemicellulose rapidly loses the side chains,

which are often acetyl groups that are condensed as acetic acid. Likewise, lignin, which has methoxy substituents on the majority of the phenylpropane monomer units, leads to the production of methanol. Prior to the advent of petrochemical synthesis, wood pyrolysis was a major source of acetic acid, acetone, and methanol; the latter, as a result, is still known as wood alcohol.

The volatile materials also undergo thermal rearrangements according to the temperature and the duration of exposure to that temperature.

Credit for Figure 1 is due to many researchers in the biomass pyrolysis field, including T.A. Milne and R. Evans, of the National Renewable Energy Laboratory (NREL) USA, and captures the changes taking place in both the solid and the gaseous phases of, for example, hardwood pyrolysis, as the severity of the pyrolysis treatment increases. In reacting chemical systems, the term, severity, is used to capture the idea that both the duration of heating and the final temperature influence the chemical products of pyrolysis. Very low severity treatments of short duration to a maximum temperature of about 250°C are sometimes called torrefaction, and result in a product that has lost some water and carbon dioxide from pyrolysis while retaining almost all of the heat value. Traditional charcoaling is a medium severity process, while the production of bio-oils is a short duration high severity process, which, if the duration at high temperature is maintained, will go all the way to gas and soot.

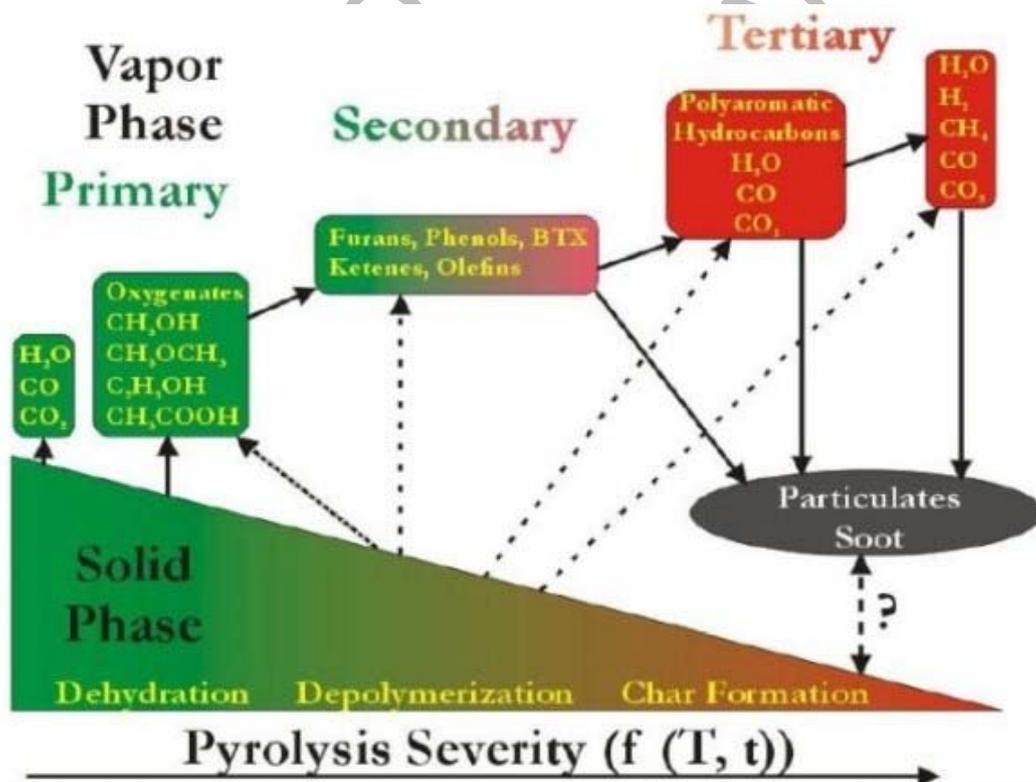


Figure 1. The primary, secondary and tertiary products of solid biomass as a result of increasing pyrolysis severity

2.2. Thermal Aspects of Pyrolysis

Most biomass has a cellular structure with extensive voids, such that while the density of the lignocellulosic cell wall material typically is between $1.5 - 2 \text{ g cm}^{-3}$, the density of wood ranges between 0.2 and 1.3 g cm^{-3} for Balsa wood and *Lignum Vitae*, respectively. More typical softwoods, such as pine, have values around 0.4 g cm^{-3} and typical hardwoods, such as oak, are about 0.6 g cm^{-3} . As a result, the heat transfer characteristics are very poor characterized by the Biot number, a dimensionless ratio of surface convective heat transfer to internal heat conductivity (see). When the Biot number is very small e.g. $< 10^{-3}$ then the material conducts heat rapidly to provide a uniform temperature throughout. However for biomass samples such as wood the Biot number often has values much greater than 0.2 , and consequently there are large temperature gradients within the solid wood material. Thus, at high external heat fluxes with large particles of $> 2 \text{ cm}$ thick, the surface rapidly reaches the external temperature, while the center of the particle is still cold. For a 1 cm^3 cube of wood, a very slow heating rate of 0.01 K min^{-1} (Biot number $\cdot 10^{-5}$) would result in an isothermal situation throughout the cube. In this case, the drying of the wood would take place independently of the pyrolysis process. Under the conditions that are often described as fast pyrolysis, the heating rates are on the order of 100 K min^{-1} . For the same 1 cm^3 cube, the Biot number 0.3 indicates a large thermal gradient, whereas a 1 mm^3 cube would more likely to be isothermal with a Biot number ~ 0.003 .

For Biot numbers around unity, the passage of the thermal wave from the outside of the particle to the center takes a relatively long time and is opposed by the diffusion of the products of drying (water vapor) and pyrolysis (organic molecules and permanent gases) migrating to the surface. Physically this separates the drying process from the pyrolysis process such that each small volume of wood polymer is totally dry when it pyrolyzes. However, the net chemical result is that the primary products of pyrolysis have close contact with char and can react with the solid char matrix, modifying both it and the composition of the tars and gases. For thermally thick samples in high external heat flux regimes ($Bi = > 10$), the processes of drying and pyrolysis travel together as a wave through the material. This pyrolysis wave is an exotherm and augments the rate of heat transfer through massive materials.

3. Pyrolysis Process Technology

Charcoal has been the major commercial product of biomass pyrolysis for a long time and is the largest single biofuel produced today. Both in historical times, and in developing countries today, relatively simple charcoal kilns have provided charcoal for use as a high quality fuel and as a reducing agent in the winning of ores. The Iron Age was characterized by the use of charcoal, and in Medieval times the increasing industrialization of society resulted first, in the over consumption of wood for charcoal production for use in iron production, and then charcoal was replaced with coke produced from coal. In Brazil charcoal is still produced from wood to produce pig iron, and in Norway wood charcoal is used in metallurgical applications, including the production of silicon for use in solar cells. Current estimates of charcoal production are around $(20 \div 25) 10^6 \text{ t}$. This can be derived from the Food and Agriculture Organization of the United Nations (FAO) forestry data, which shows world charcoal production at $137 10^6 \text{ m}^3$ as solid fuelwood equivalent; and

using a conversion of 6.0 m³ fuelwood per 1 t of charcoal, the yield is 23 10⁶ t. Additional charcoal is derived from wood that is not from forests (a weakness in the FAO forestry data base) and non-woody biomass. Globally the primary energy input required to manufacture about 700 PJ of charcoal is approximately 3 EJ of fuelwood.

The off gas and liquids represent as much as 40% of the original energy of the wood. In simple charcoal making, these are often not utilized, creating pollution of the soil, water and air. In the larger industrial systems, the recovery of byproducts for sale may not be economic compared to fossil-fuel derived products; however, the fuel value of both the gas and the tars (sometimes called pyroligneous liquids) may be utilized in the carbonization process to reduce energy loss, increase efficiency, and eliminate pollution. The destructive distillation of wood in retorts, prior to the coal and petroleum eras, provided a wide range of chemicals, in addition to the valuable charcoal, by condensing the liquids from the pyrolysis process. Before there was extensive chemical synthesis of methanol and acetic acid from fossil fuels, these were both byproducts of charcoal manufacture. Typical mass yields of charcoal and byproduct chemicals for Beech (*Fagus sylvatica*) are: charcoal - 32.5%; gases (with a heating value of 9 MJ Nm⁻³) ¥ 16%; tar - 14%; acetic acid - 7.7%, and methanol - 2.1% . Charcoal has value not only as fuel and metallurgical reducing agent, but is also the base for the production of special carbons in gas and liquid absorption applications. So-called activated charcoal is charcoal that has been chemically treated at high temperatures to produce an almost pure carbon product with a very high surface area. The absorptive capacity as a result of the large surface areas (e.g., 10³ m² g⁻¹) is extremely large and can trap a wide range of toxic substances and vapors.

3.1. Slow Prolysis

Although pyrolysis has been used over a long period of time, the processes taking place during pyrolysis were not understood. This had to await the 20th Century evolution of polymer science and the application of rapid analysis techniques tools. Figure 2 is a summary of the extremes of pyrolysis behavior of lignocellulosic materials. The products of pyrolysis are the char, gases, and liquids, which are composed both of condensed water and the oils or tars from the pyrolysis process.

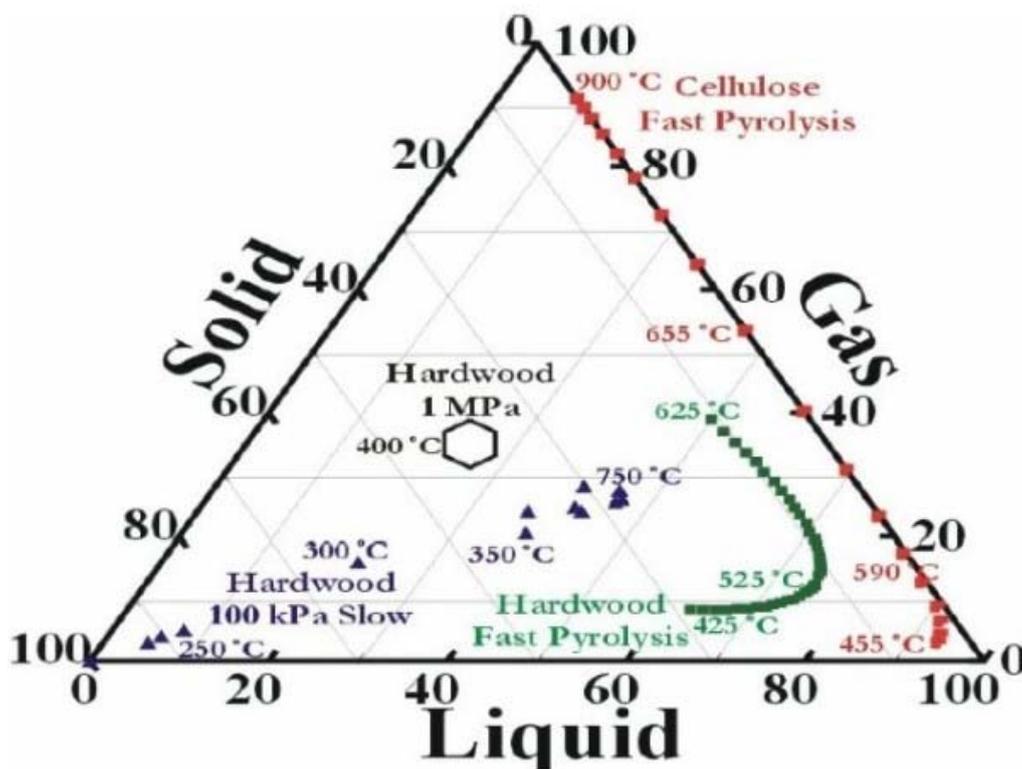


Figure 2. Product gas, liquid and solid ratios as a function of pyrolysis process conditions

The triangles show the progression of traditional slow pyrolysis of a hardwood in a retort that collects the liquids and gases from the process. Starting with 100% solid material as unconverted hardwood at ambient temperature, by 250°C the solid mass is at 88%, less than 10% liquid, and only a few percent gas. Between 300°C and 350°C, the pyrolysis wave typically starts to move through the mass of the biomass, and the char rapidly decreases to less than 60% of the mass, the liquids are 20% to 30%, and the gases are between 15% and 25%. The char at this stage is not a pure carbon and contains both oxygen and hydrogen. Further heating of the char to 750°C will decrease the mass of the char, and while its composition moves closer to pure carbon, the yield of gas increases and that of liquids decreases. Typically the pyrolysis is conducted for hours to a maximum temperature of 400°C - 500°C. The charcoal yield is 35% to 40% by weight. The central hexagon shows the theoretical yields of solid char, liquid as water, and gases (mainly methane and carbon dioxide) under the conditions of slow pyrolysis. Until recently it was thought that the theoretical yield was not attainable; however, studies by Professor Antal, at the University of Hawaii, and colleagues from around the world have demonstrated that high pressure carbonization conducted in a retort at 1.0 MPa pressure and a temperature of about 400°C will produce almost the theoretical yield; this process is now being commercialized. The high pressure restricts the vaporization and diffusion of the liquid products of pyrolysis out of the body of the pyrolyzing biomass, allowing them to react in the char matrix to produce more char, water and permanent gases.

The slow pyrolysis process is an example of the pyrolysis wave phenomena in massive biomass, such that the only requirement is for the initiation of the process in which a small

proportion of the wood charge is burnt to provide the initial heat in a well insulated reactor. Charcoal manufacture ranges from the artisanal methods of the earth pit or mound, to extremely high technology processes such as the Lambiotte continuous retort. The majority of industrial charcoal is produced in brick kilns, of which the Argentine half-orange and the Brazilian beehive are major examples. Portable steel kilns and permanent concrete kilns with rectangular steel doors are also used; these are sometimes called Missouri kilns. The capacities and throughput of the different systems are shown in Table 1.

Charcoal Kilns					
Technology	Production Cycle		Performance Data		
	Volume (m ³)	Days	Production (tonne)	Efficiency tropical wood/tonne of charcoal	Annual production (tonne)
Earth Pit	26	60	6	4.5	18
Mound Cassemance	100	24	12	5.5	144
Brick - Argentine	50	14	9	3.75	180
Brick - Brazilian	45	10	5	2.8	175
Missouri Kiln	180	25	20	3.0	240
Lambiotte	130	Continuous		2.8	2500

Table 1. Charcoal production systems

The global average efficiency of charcoal production is about 30%. However, this ranges from 25% in Africa, which uses mainly artisanal methods, to 48% in Latin America, which uses industrial kilns. Artisanal methods include the pit and mound methods in which the dry wood to be charcoaled is placed, and then covered with earth to both insulate the reacting wood and to prevent the access of air. One of the oldest illustrations of this technique is by Agricola in his multi-volume work, *De Re Metallica*, published by Froben and Episopus in Basle in 1556.

3.2. Fast Pyrolysis

Fast pyrolysis to produce bio-oils began only 25 years ago, following the development of analytical methods that made it possible to work with very small sample sizes in pyrolysis studies and ensure that heating of the biomass was uniform throughout the mass of the material. These techniques included: thermogravimetric analysis at very small scales, Fourier transform infra red spectroscopy, mass spectrometry, gas and liquid chromatography, as well as detailed simulation models. The rate of heating and the removal of the small molecular weight materials were also important. With these advances, it was realized that the scientific understanding of man-made polymers could be applied to the

natural polymers in biomass. Earlier efforts had been confounded by the interactions between the highly reactive pyrolysis products and the still solid partially reacted materials. By designing processes with relatively small particles and heating them up rapidly by means of so called *Fast Pyrolysis*, it was possible to convert the majority of the input biomass material not into charcoal and gases, but into a reactive liquid (sometimes called bio-oil) by rapidly quenching the vapors from the pyrolysis process. This is illustrated with the square symbols in Figure 2, showing the high yields of liquids around 525°C during the pyrolysis of a hardwood. Over 75% of the original mass is converted to a liquid that contains about 10% water. This result, which is far from the predicted chemical equilibrium shown by the hexagon in Figure 2, has spawned new applications of biomass pyrolysis. The final curve on Figure 2, is for the rapid pyrolysis of a pure form of cellulose that has been chemically isolated from wood. At 455°C the yield of liquid is well over 90%, and as the temperature is increased to 900°C, there is hardly any solid char and the liquid is converted into gas. At around 600°C a major component of the pyrolysis liquid from cellulose is levoglucosan, as would be expected from the normal thermal breakdown of a glucan chain.

3.2.1. Fast Pyrolysis Process Developments

There are several fast pyrolysis processes under development and in the process of commercialization, with the goal of providing a liquid fuel from lignocellulosic biomass that can substitute for fuel oil in any static heating or electricity generation application. The liquid can also be used to produce a range of speciality and commodity chemicals. The essential features of a fast pyrolysis process are:

1. very high heating and heat transfer rates, which often require a finely ground biomass feed;
2. a carefully controlled reaction temperature of around 500°C in the vapor phase and residence time of pyrolysis vapors in the reactor less than 1 s; and then
3. quenching (rapid cooling) of the pyrolysis vapors to give the bio-oil product.

The main product, bio-oil, is obtained in yields of up to 80 wt% of dry feed, together with by-product char and gas, which are available for use as energy sources within the process so there are no waste streams.

In order to meet the time and temperature configuration, a wide range of reactor configurations have been tested and operated. Bubbling fluid beds are the most popular configurations due to their ease of operation and ready scale-up. There are several companies that are developing this type of operation including Union Fenosa in Spain, Dynamotive in Canada, and Wellman in the UK. Circulating fluidized beds (CFB) and transported bed reactors have been developed and commercialized by ENSYN (USA) and are used in the USA for the production of food flavorings and related products by the Red Arrow Company of Wisconsin in several plants. An alternative approach has been ablative pyrolysis, in which much larger particle sizes can be employed than in other systems, as the heat is transferred from a hot surface to the biomass particle and the process is limited by the rate of heat supply to the reactor rather than the rate of heat absorption by the pyrolyzing biomass. Much of the pioneering work on ablative pyrolysis reactors has been

carried out by J. Diebold and colleagues at NREL in their vortex reactor, in which centrifugal force is used to hold a massive particle of wood against an externally heated wall. An alternative device that combines both hot surfaces and an inert heat carrier is the rotating cone reactor, originally developed at the University of Twente, which has been scaled up and implemented as a pilot unit in Shenyang Agricultural University (Peoples Republic of China) by the Biomass Technology Group in the Netherlands. Commercialization of bio-oil as a fuel is underway with Fortum in Finland.

Though often included in discussions of fast pyrolysis by virtue of its high liquid yields, vacuum pyrolysis is not a rapid heating technique and is in the same thermal regime of time and temperature as slow pyrolysis charcoal production; however, yields of liquid that are over 50% of the original biomass are achieved by removing the vapors as soon as they are formed by operating under a partial vacuum - essentially the converse of work at high pressures, in which the liquids are held in the charring mass to increase the yield of char.

3.2.2. Bio-oils from Fast Pyrolysis. Properties and Applications

The bio-oil is a treasure trove of chemicals in addition to being a fuel. Extensive work at NREL in the USA has developed the application of the phenolic and neutrals extracted from the bio-oil as a phenol substitute in phenol formaldehyde resins used to make plywood and oriented strandboard. Red Arrow in the USA uses the ENSYN process to produce smoke for food flavoring and food colorings. There is also potential for specialty chemicals production. The wide range of chemicals in the bio-oil and their reactivity with one another, result in slow polymerization of the oil over time. Currently there is work underway to improve the storage characteristics, especially under moderate to high temperatures.

The energy applications of the bio-oil are predicated on the concept that there will be centralized production of the oil at a location close to where the biomass resource is available and that it will be shipped by tanker to an end user. Since the oil has a density of about 1200 kg m^{-3} and a slightly higher energy content than wood, which in chip form has a density of $400 \text{ to } 600 \text{ kg m}^{-3}$, the distance over which it can be transported is clearly superior to that of wood. The application of the oil in existing commercial facilities with only minor modification is attractive, again compared to having to invest in biomass-specific facilities. Current end-use possibilities are as a boiler fuel for stand-alone heat or in combined heat and power (CHP) using the steam cycle after either diesel or gas turbine electricity generation. The majority of these options have now been demonstrated to be technically feasible.

3.2.3 Economics and Environment, Health and Safety (EH&S) of Bio-oils

Since fast pyrolysis processes are carried out at essentially atmospheric pressure and the temperatures are well within the capabilities of conventional metals, the capital investment in the processes is moderate. Detailed cost analyses have been carried out for several size ranges of process, and the PyNe Network (www.pyne.co.uk) has published generalized curves that result in a cost equation of the form:

Cost (ECU GJ⁻¹) = 8.87*(wood capacity [dry t h⁻¹])^{-0.3407} + 0.09*(feedcost[ECU dry t⁻¹])¹
 This equation assumes that the lower heating value (LHV) of the wood feedstock is 18 GJ t⁻¹. For a modular plant of 5 t h⁻¹ throughput and a zero cost feedstock, the cost of the oil is about 4.5 \$ GJ⁻¹. For a feedstock costing around 31 \$ t⁻¹, the cost of the oil would be 7.3 \$ GJ⁻¹.

The PyNe Network also maintains an EH&S working group to assist in the safe deployment of bio-oils. The oils are recognized as being toxic, mainly because of the low pH and high concentrations of phenolic compounds, which can cause eye damage but not skin damage, and have been demonstrated to be non-mutagenic. Despite the oils being complex mixtures of at least 74 different compounds, Material Safety Data Sheets have been produced for the oils and, subject to reasonable precautions, the materials have been extensively shipped. Full protocols need to be developed for equipment cleaning, the management of accidental spills and to ensure compliance with all EU shipping and handling regulations.

4. Gasification Technologies

The conversion of biomass into a gaseous fuel opens up modern applications in electric power generation, the manufacture of liquid fuels, and the production of chemicals from biomass (Figure 3).

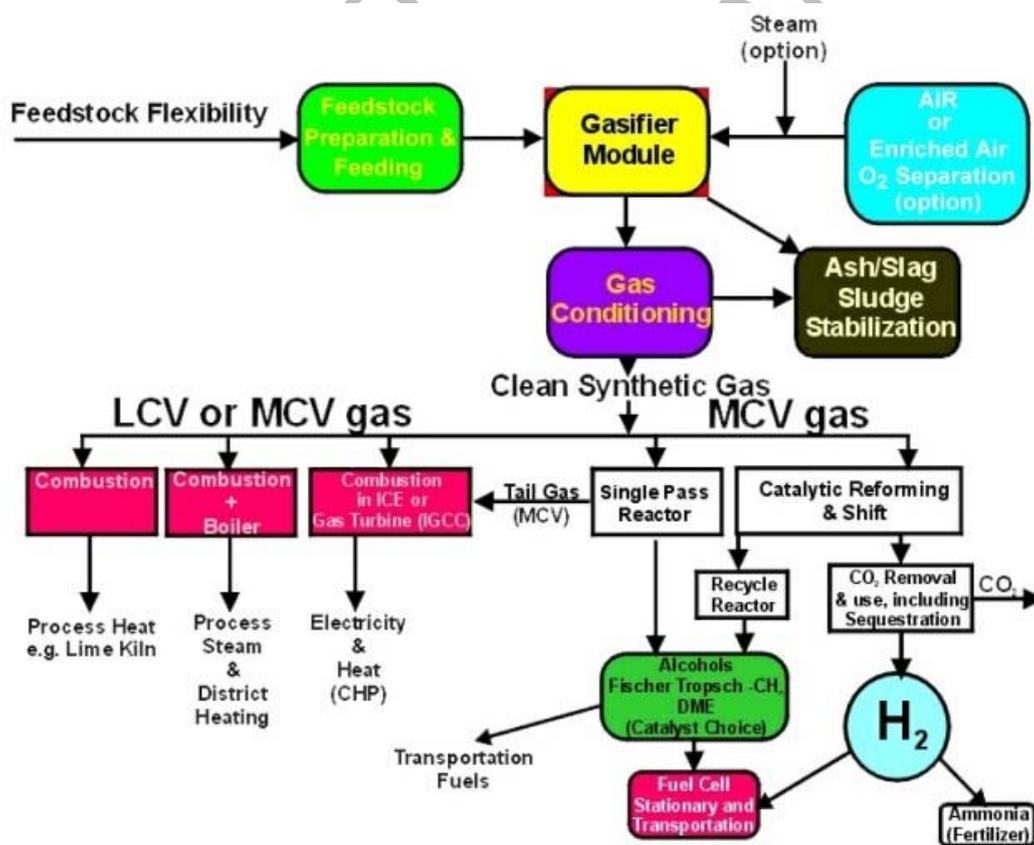


Figure 3. Gasification process and product characterization

The process is feedstock flexible. The feedstock can contain organic rich materials from urban residue stream, industrial and commercial operations, agriculture/food processing, black liquor, forest residues, and energy crops. At the contrary the biotechnology route to gas from biomass is based on anaerobic digestion, and this has substrate specificity that restricts it to biomass feedstock that can be easily hydrolyzed to sugars, amino acids, small lipids, alcohols and fatty acids.

4.1 Gasification Fundamentals

Gasification is an extension of pyrolysis; however, now the thermal process is optimized to give the highest yield of carbon and energy in the gas phase, rather than to produce a char or a liquid. The majority of gasifiers are partial oxidation reactors, in which just sufficient air or oxygen is introduced to burn part of the input biomass to provide the heat for pyrolysis and gasification. If the oxidant is air, the product gas is diluted by the nitrogen present, and although air is 79% nitrogen, the stoichiometry of partial oxidation is such that the final product gas has about 50% nitrogen as a diluent. As a result the gas heating value of the fuel gas derived from air driven partial oxidation gasifiers ranges from 4 - 6 MJ Nm⁻³. The value can be higher if the feedstock is very dry, thus minimizing the heat demand for the process and the amount of oxidant required. If the processing strategy optimizes the higher heat content, production of gases such as methane, the two and three carbon hydrocarbons, and olefins, further increases the calorific value. The energy content of the typical gases produced in biomass gasification is shown in Table 2. The use of pure oxygen as the gasification agent eliminates the nitrogen diluent and can produce medium calorific value (MCV) gases in the range of 10 - 20 MJ Nm⁻³. An alternative strategy is to carry out the gasification process by means of indirect heat input. In this case the product stream is even higher in calorific value, as neither nitrogen nor the carbon dioxide produced from the combustion *in-situ* of the partial oxidation processes is present in the product gas stream. The challenges to achieve a clean and useable fuel gas have been addressed through gasifier design and post-gasification processing to remove tar and particulate contaminants from the gas stream.

Gas	HHV	LHV
	MJ Nm ⁻³	
Hydrogen	12.77	10.80
Carbon monoxide	12.65	12.65
Methane	39.79	35.86
Ethane	70.39	64.45
Propane	101.73	93.68
Butane	132.37	122.27

Table 2. Heating values of fuel gases^a

4.2. Gasifier Systems

The main challenge in gasification is enabling the pyrolysis and gas reforming reactions to take place using the minimum amount of energy in reactors that are economical to construct. With a history going back to the late 18th Century, there have been an extraordinary number of different designs and process configurations. Prior to the development of fluidized bed technologies in the 1920s, the majority of the gasifiers were so called fixed bed units. The flow of gasifying agents, usually air and steam, could be co-current with the biomass feed, or counter-current; these are often described, respectively, as downdraft and updraft gasifiers. Downdraft gasification was widely used during the Second World War as an on-board fuel gas generator to offset the lack of gasoline. Millions of units were constructed and then abandoned as soon as petroleum supplies resumed. Units derived from the automotive application are marketed today as stationary generating sets, equipped with internal combustion engines (ICE) with either spark ignition or diesel pilot ignition, for power production in remote locations and in developing countries without grid systems.

4.2.1. The Counter Flow Moving Bed Gasifier (updraft)

The simplest and oldest form of gasifier is the counter flow moving bed design, also known as the updraft reactor. The system, diagrammatically shown in Figure 4, consists of an insulated shaft into which the feedstock (typically pieces larger than 3 cm on a side) is fed.

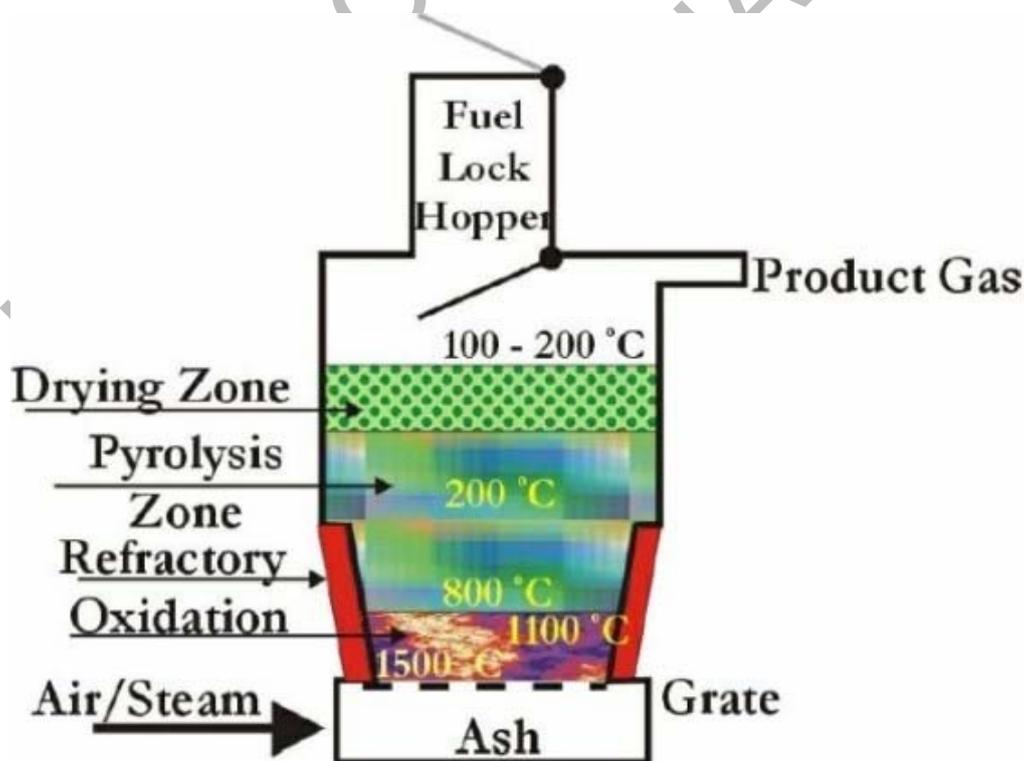


Figure 4. Counter flow (up draft) gasifier schematic

An exception is the use of rice hulls, which have excellent flow characteristics despite their small size. With very large diameter units, the pieces can even be logs of wood with 1 m length and 20 cm diameter. The shaft is filled to a depth of 0.5 to 2 times the vessel diameter, and the mass of material is supported on a grate. The oxidant (air or enriched air/oxygen) and sometimes steam are introduced, and the biomass is ignited at its base.

This burns the material and the hot gases flow up through the bed, exchanging heat with the down flowing biomass material and, at the same time, pyrolyzing and drying the input. At steady state the bed is maintained by continuous additions of the feed, and the heat requirement is met by the combustion of the pyrolyzed and charred input material at the grate. The product gases have exit temperatures that are often less than 250°C and include the desired fuel gases (methane, carbon monoxide, hydrogen, and C₂ hydrocarbons), nitrogen, carbon dioxide, and water vapor. The latter arises from both the moisture content of the feed and the products of combustion. The gas also contains several percent of condensable tars, which consists mostly of primary and secondary pyrolysis products in quite high concentrations. This arrangement is very efficient in converting the material to gas, and the only solid residue is the mineral matter in the biomass. As the temperatures in the combustion zone can be very high, there may be problems with the formation of slag: molten mixtures that can impede the oxidant flow. Some of the systems are constructed deliberately to form a molten ash or slag, and handle this by dropping the slag into a receiving tank where it solidifies and shatters to an easily handled aggregate. A system known as the Purox system was developed in the 1970s to handle urban wastes using oxygen as the oxidant.

The throughput of air-based systems is relatively low, handling about 150 kg h⁻¹ of dry biomass per square meter of the gasifier cross-section. This operational limitation is due to the reduction of the rate of heat generation at the grate to avoid slagging in dry systems.

The lower throughput rate also helps to manage the problems of maintaining a uniform flow of the descending material to avoid channeling and even greater reductions in throughput. The largest units are typically 3 - 4 m in diameter and handle between 50 and 100 t d⁻¹ of material with a rating of 10 - 20 MW (th) input. The hot gas efficiency can be as high as 80% conversion of the input energy into a fuel gas and sensible heat. On cooling, the cold gas efficiency will be about 70%.

If the gas is maintained at high temperature and then fired in a kiln or boiler, the presence of tars and particulate are of little consequence, as the tars are combusted in the excess air and the particulate is removed in the kiln exhaust or boiler flue gas system. Such close-coupled systems are quite common applications of biomass gasification in several industries and the basis of district heating systems used in Finland.

The gas typically has a heating value of 6 MJ Nm⁻³ on a dry basis, and is richer in methane, ethene, and ethyne than most other systems. For engine applications the gas has to be cleaned up and cooled to ambient temperatures. Typically this is done with some sort of scrubbing system (e.g., a wet electrostatic precipitator) to remove tar and particulate matter, and the tar/water removed has to be separated and then treated for release to the environment.

4.2.2. Fluidized Bed Gasifiers

Fluidized beds can remove the grate limitation of the moving bed gasifier, since, due to their high mixing rates and outstanding heat transfer rates, they can achieve through-puts of over $1500 \text{ kg m}^{-2} \text{ h}^{-1}$ of dry biomass. There are two modes of fluidized bed operation: bubbling (Figure 5), and circulating (Figure 6).

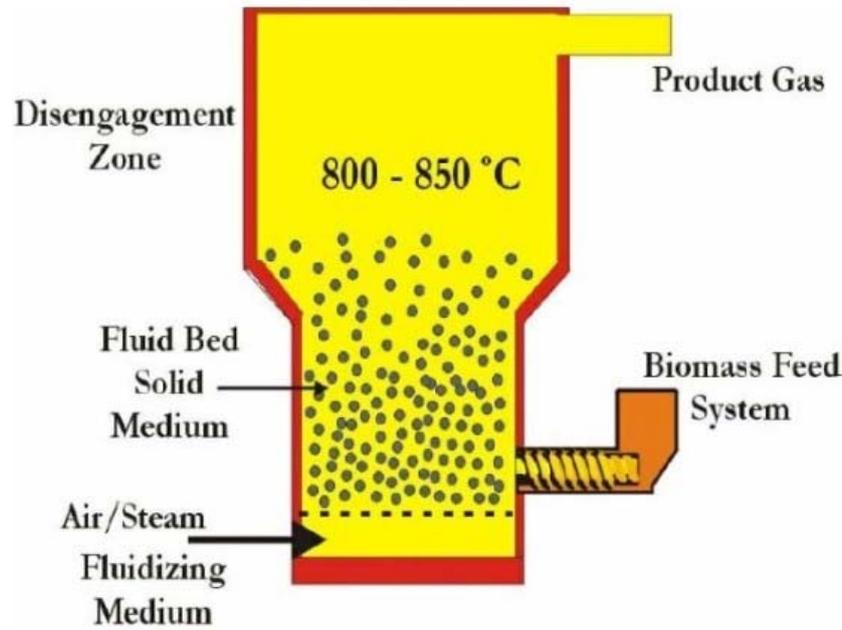


Figure 5. Bubbling fluidized bed (BFB) gasifier

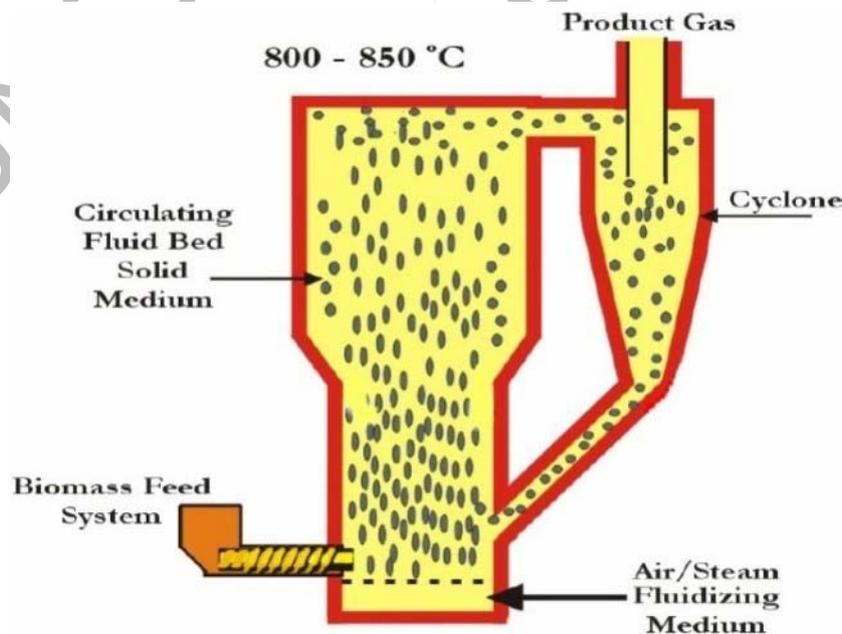


Figure 6. Circulating fluidized bed (CFB) gasifier

In a bubbling fluid bed (BFB), the inert fluid bed medium (silica sand, dolomite, alumina, and olivine) is retained in the body of the bed, which is expanded and in motion (literally bubbling) due to the flow of the fluidizing gas medium into the bed. The terminal velocity of a particle in the flow is still higher than the linear flow rate of the gas, and thus the particle remains in the body of the unit. In the CFB, the gas flow is increased to the point that the terminal velocity of the particle is exceeded and it is transferred out of the expanded bed and captured in a cyclone for return to cycle. The effective rating of a 3 m diameter unit is over 50 MW (th) input of biomass. Since the combustion process and the pyrolysis process are now mixed, the exit gas temperatures are typically 700°C – 800 °C.

Due to cracking processes, the tar production is lower and mainly composed of secondary and tertiary tar components; however, the tolerance of high moisture content feedstocks is much more limited than the counter flow moving bed unit. The system design is also more complex, requiring blowers to inject the oxidant at the base of the fluidized bed. In addition to the expansion of the gas due to temperature, there is also an increase in the gas volume due to the formation of the fuel gas. This necessitates careful design of both the CFB and the freeboard in a BFB, while in a CFB this is accommodated by the fact that the entire bed is in circulation. The oxidant requirement is typically 0.3 kg O₂ per kg of dry feedstock.

4.2.3. Entrained Flow Gasifiers

The highest reactivity systems are entrained flow units, in which the feedstock is finely divided and burnt in a sub-stoichiometric flame at high temperatures. The post-combustion gases are then allowed to reach chemical equilibrium before being quenched. Such units produce very few higher hydrocarbons and tar materials. The challenge for biomass is to obtain a sufficient rate of fuel injection to the flame. One configuration is the Koppers Totzek gasifier. For fossil fuels, the Texaco gasifier uses a dense slurry of coal or petroleum coke in water as the feed to a pressurized oxygen flame, producing a hydrogen and carbon monoxide mixture for use as a syngas or as a fuel in gas turbines. There are no current applications of entrained flow biomass systems.

4.2.4. Co-current Moving Bed Gasifiers (downdraft and cross draft units)

These gasifiers were widespread during World War II (various estimates put the number at over one million). They were used to convert biomass or charcoal into a fuel for gasoline vehicles in periods of great shortages of transportation fuels. The same co-current principle is the basis of many of the gasifier engine generator sets that are being marketed today in China, India, and other developing countries for village and industry power. Like the other gasifiers described above, the design is a partial oxidation system. The physical arrangement is a shaft reactor, into which the biomass is introduced at the top, Figure 7. The material then flows down to an oxidation zone, which feeds heat back to the incoming biomass to pyrolyze the material into gases, tars, and charcoal. The charcoal is partially combusted in the oxidation zone, and the products of pyrolysis flow through the incandescent combustion zone to be cracked into, primarily, hydrogen and carbon monoxide as the fuel gases, with little or no tars passing through.

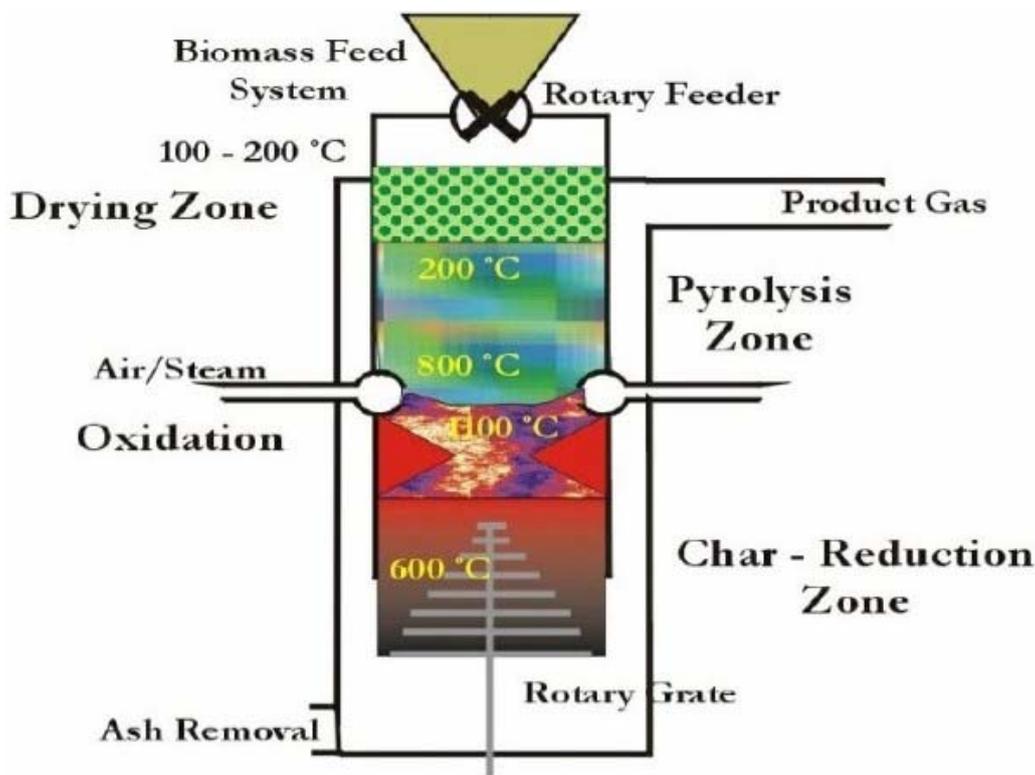


Figure 7. Co-current (down-draft) gasifier schematic

The combusted gases flow on through the hot charcoal, reacting with it, until the rate of reaction effectively goes to zero, as the reactions are in fact very endothermic. The net result is a gas that is very low in condensable tars, and except carbon dioxide, water vapor, and nitrogen, the fuel gases are mainly hydrogen and carbon monoxide. The low tar production is the reason that this was the favored system for on-road vehicles in the 1940s. Like all moving bed reactors, the operation depends on there being an adequate void space between particles. The wood feedstock has to produce a char, which has sufficient strength to support the column of feedstock without crushing and blocking the flow. The overall efficiency is lower than the counter flow system for two reasons. Chemically it is not possible to fully convert the charcoal; and the sensible heat from the combustion zone is not transferred to the incoming feed material, but has to be heat exchanged with air oxidant prior to being quenched. Because of the need for uniformity of mass and heat transfer in the high temperature reaction zone, the diameter of such units is generally limited to less than 1.5 m, and with typical throughputs of $300 \text{ kg m}^{-2} \text{ h}^{-1}$ of dry biomass, the capacity of units ranges from 100 kW(th) to 2 MW(th) input. The chemistry of this gasifier is significantly different from the other gasifiers, which have very high burdens of liquids such as tars in the product gas. In this case the primary and secondary pyrolysis products are mixed with oxygen and burned prior to passage over the hot charcoal (Table 3, Reaction 1). The net result is that the chemistry has much more in common with a blast furnace for reducing iron. The main fuel gases are H_2 , CO , and CH_4 produced in the reaction steps 2 – 5.

Summary Reaction Steps	Results Produced
Generation of pyrolysis gases and char from biomass	
0	Biomass ($\text{CH}_{1.4}\text{O}_{0.6}$) + Heat \rightarrow Char (C(s)) + Pyrolysis gases
Primary and secondary pyrolysis products, mixed with oxygen and burned prior to passage over hot charcoal	
1	Pyrolysis gases + $\text{O}_2 \rightarrow$ $\text{CO}_2 + \text{H}_2\text{O} + \text{CH}_4 + \text{CO}/\text{H}_2 + \text{Heat}$
Solid carbon reactions	
2	$\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$
3	$\text{H}_2\text{O} + \text{C} \rightleftharpoons \text{CO} + \text{H}_2$
4	$2\text{H}_2 + \text{C} \rightleftharpoons \text{CH}_4$
5	$\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H}_2$

Table 3. Sequence of reactions in co-current gasification

The solid carbon reactions after the injection of air/oxygen result in the fuel gas mixture shown in the reaction steps 2 - 5. Each of these reactions is, in fact, composed of multiple steps. They are also equilibrium reactions so that, in the water gas shift (Table 3, Reaction 5), an excess of steam in the presence of carbon monoxide will form hydrogen; and the reverse is also true, in that a mixture of carbon dioxide and hydrogen will form carbon monoxide and water. The position of the equilibrium is determined by the concentrations of the reactants and the temperature, such that at low temperatures, the production of hydrogen is favored, and at high temperatures the production of carbon monoxide is promoted. The key reactions that form the product fuel gas from the solid carbon are very endothermic, and the result is that at about 500°C, though the equilibrium is still favorable, the rate of the reactions on the solid carbon are extremely slow. As a result these type of co-current gasification systems always produce excess char in addition to the product gases.

4.2.5. Indirect gasifiers

Medium calorific value (MCV) gas can be produced, allothermally, that is, without using oxygen in auto-thermal (partial oxidation) gasification. This requires an external source of heat to be transferred to the biomass to pyrolyze the feedstock under conditions of high severity, i.e., long residence times at high temperatures. To this end there have been proposals to use concentrated solar energy, or to use high temperature nuclear reactors as the heat source in the gasification of a wide range of feedstocks. In the case of biomass the pyrolysis gasification process will provide a char stream, as can be seen in Figure 2, with either slow or fast pyrolysis to temperatures of 600°C – 750°C, in amounts representing between 12% and 25% of the input biomass. This contains sufficient energy to drive the pyrolysis process. There are a number of developments that are already in the demonstration phase in which biomass is pyrolyzed using a solid heat carrier in an inert atmosphere or steam or product MCV gas to generate the MCV fuel gas and char. The char and the cooled heat carrier, which can be silica sand, alumina, or a mineral such as olivine are then transferred to a separate air combustion unit. Here the char is combusted to heat up

the heat carrier, which is then returned to the pyrolysis gasification unit. This is shown diagrammatically in Figure 8. There are mechanical separation and isolation devices in the heat carrier circulation loops that prevent the passage of fuel gas from the gasifier to the oxidation conditions of the combustor. The transportation mechanism is via fluidization of the heat carrier. To this end, a group in Austria constructed a version with a CFB combustion unit and BFB pyrolysis gasifier; and in the USA, units have been constructed with a CFB pyrolysis reactor and a BFB combustor as well as a dual CFB configuration that was scaled up to 60 MW(th) biomass input. Another variant, developed by Manufacturing and Technology Conversion International, Inc. (MTCI), a U.S. company, was a BFB pyrolysis and steam char reaction system with the heat supply from immersed heat exchanger bundles in the bed. The heat exchanger bundles are fueled with part of the product gas, and the char from pyrolysis is consumed, as in the co-current gasifier by means of the reactions steps 2 – 5, described above.

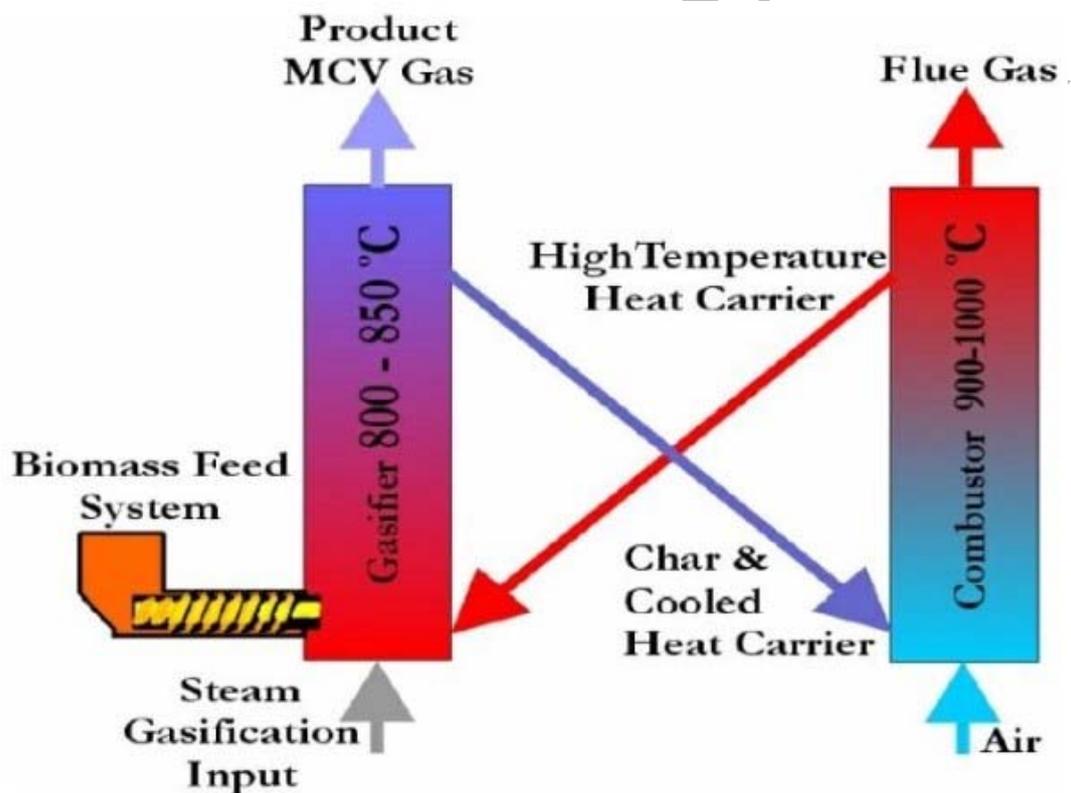


Figure 8. Indirect gasification using a solid heat carrier schematic

4.2.6 Black Liquor Gasification

A major gasification opportunity resides with the kraft pulping industries of the world. Chemical processing to produce 103 million t of pulp annually generates between 60 and 80 million t of by-products, which are used to generate energy for the process and to recover chemicals. After satisfying the in-pulp mill energy needs and chemical recycling requirements, studies at NREL and elsewhere have identified an additional export potential of about 1.4 MWh per 1 t of air dry pulp produced if present day boiler systems were to be replaced by high efficiency gasification combined cycle cogeneration systems. The

worldwide potential is, therefore, on the order of 140 TWh electricity generation, representing about 1% of the global power production of 15 PWh from all sources in 1999. Present day electricity production from biomass (classed as combustible renewables and waste in the IEA statistics) is about 160 TWh.

The present day chemical pulping process uses a complex combustion system called a recovery boiler to generate process heat and electricity as well as to recover the processing chemicals in an almost closed cycle, shown in Figure 9. The recovery boiler is a very complex device, which is actually operated as a gasifier - combustor. After evaporation of the majority of the water, the very high solids black liquor is sprayed onto a mass of char in the bottom of the boiler.

The lignin pyrolysis produces reducing gases and char. These react with the spent pulping chemicals to produce sodium carbonate and sodium sulfide. Ash and other minerals in the wood feed turn up as non-process elements and have to be removed from the cycle. The gases from the char bed pass to an oxidizing zone in the furnace and burn to produce process steam (and electricity) as well as provide radiant heat back to the char bed for the reduction chemistry to take place. The product chemicals are molten, drained from the char bed to collectors, and then poured into water to produce green liquor.

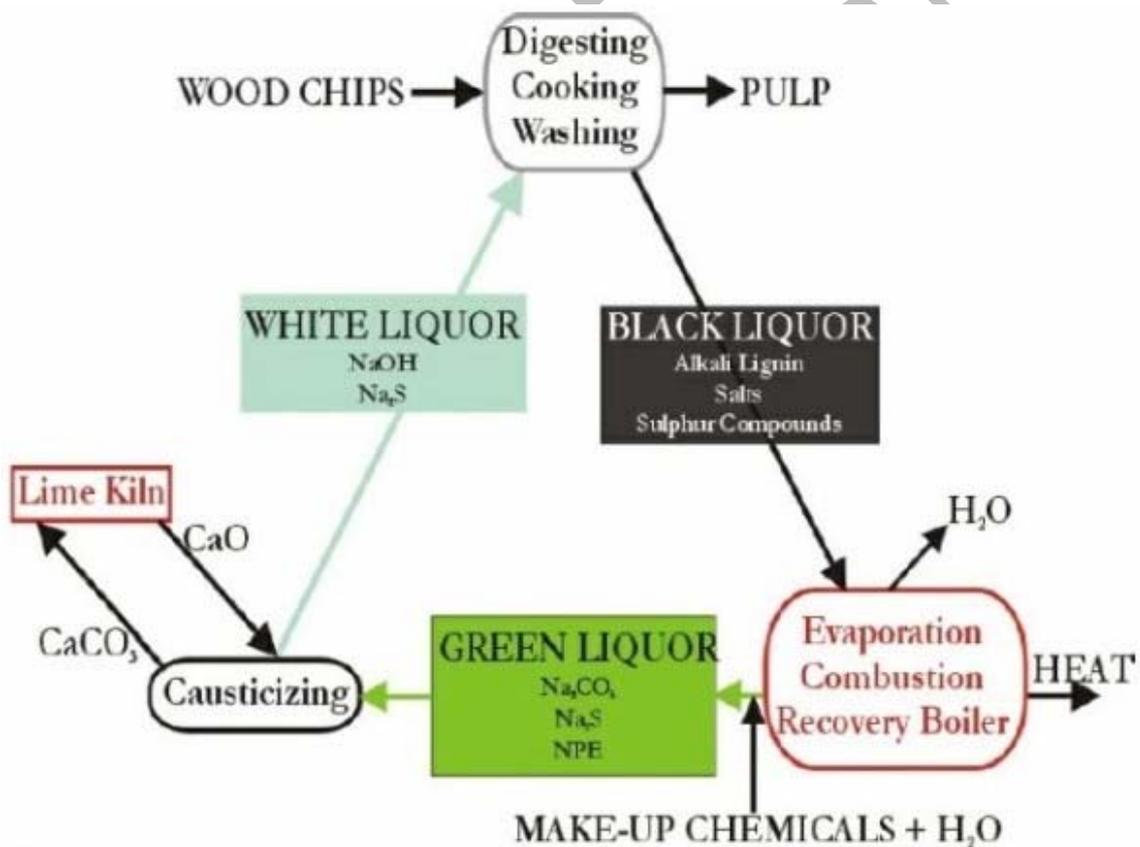


Figure 9. Black liquor in the kraft pulping cycle

The pulp and paper industry has a number of problems with its existing chemical pulping systems. First, in North America and Scandinavia, the current fleet of chemical recovery

boilers is aging, causing high maintenance costs. Second, these costs are compounded by air emissions rules on cluster emissions and the requirement for the installation of Maximum Achievable Control Technology (MACT) by 2006, which calls for a reduction of hazardous air pollutant (HAP) emissions by 98%. Third, there are safety hazards of operating conventional recovery boilers due to inadvertent explosions when the molten smelt and the input black liquor are mixed. And the fourth problem is the increasing electrical demand of the industry. All of these can be addressed by gasification systems, which would reduce emissions, provide the opportunity for efficient combined cycle operation to increase the electrical generation per unit of biomass, and eliminate the explosion hazards.

Gasification, as a solution to this challenge, has been in research and development since at least 1982, when initial attempts were made in the USA to develop an airblown gasifier with a molten smelt system. In Sweden an air/oxygen gasification system was introduced to boost the capacity of an existing recovery boiler that was otherwise limited by the char reduction system capacity.

This system has many similarities to the Kopers Totzeck gasifier in that oxygen is used to “burn” the black liquor in a sub-stoichiometric flame at high temperature. The product gases are then immediately quenched with water to recover the chemicals, and the gas is then injected as fuel into the existing boiler, increasing the steam output so that the mill can increase its capacity. The booster systems are at atmospheric pressure, which makes them very large for their throughput. The current R&D emphasis by the Swedish company, Chemrec, is on pressurized systems, as high as 30 bar, which will replace the entire boiler cycle.

A low temperature option that has to avoid the production of a smelt, is a version of the indirectly heated fluidized bed developed by MTCI and is described above. This unit has high heat transfer rate pulsed combustors in the fluidized bed that is made up of a sodium carbonate solid medium. This grows as the black liquor is added and a portion of the bed material is withdrawn continuously to recycle sodium carbonate to the process. The product gas is almost entirely hydrogen, carbon dioxide, carbon monoxide, and hydrogen sulfide in addition to steam. The scrubbed gas (H_2S is recycled to the process) is a medium heating value gas at about 10 MJ Nm^{-3} and can be compressed and used in a combined cycle. Since the steam gasification of char is an endothermic process, the residence time of the carbon in the system is very long, resulting in large vessels.

4.3 Applications of Gasification

Figure 3 also shows the pathways for the use of gas from gasification processes. The low calorific value (LCV) gases produced from air gasification of biomass can be used to fire boilers (directly), as well as kilns, and will generate power in ICEs and gas turbines. The MCV gas has a wider range of applications: production of chemicals, liquid fuels, and hydrogen. After its purification, these are produced from the syngas via catalytic conversion. Much of the interest in the last two decades has been in the production of electricity, as current Rankine cycle biomass-to-electricity systems are relatively low efficiency.

4.3.1 Power Systems

The work on biomass power systems using biomass gasification has followed two divergent pathways, which are a function of the scale of operations. At sizes much less than 1MW, the preferred technology combination today is a moving bed gasifier and ICE combination, while at scales much larger than 10 MW, the combination is of a fluidized bed gasifier and a gas turbine. Larger scale units than 25 MW would justify the use of a combined cycle, as is the practice with natural gas fired gas turbine stations. In the future it is anticipated that extremely efficient gasification based power systems would be based on a combined cycle that incorporates a fuel cell, gas turbine and possibly a Rankine bottoming cycle. Preliminary studies and small demonstrations have shown that it is feasible to achieve almost 70% fuel to electricity efficiencies with fuel cell systems when the fuel cell operates at high temperature as either a molten carbonate fuel cell, or as a solid oxide fuel cell (see.....) with internal reforming when the fuel is natural gas.

The small-scale units share their evolution with the vehicle gasifiers of the 1940s and the key development challenge, both then and now, is in providing a clean gas that does not reduce the lifetime of the ICE or increase its maintenance costs. An additional constraint in the 21st Century is the handling of condensates and other products of gasification that have potential environmental impacts. At the large scale, the challenge has also been in gas cleaning; in the case of the LCV gas systems, there is a need to retain the enthalpy of the gas stream so that hot gas cleaning is required. This obviates the need for condensate production, but may require advances in high temperature filtration to ensure that particles and alkali metals do not reach the high temperature sections of gas turbines, as this causes erosive wear and metallurgical corrosion. In the case of the MCV gas, the energy penalty of cooling the gas prior to cleaning it is relatively small. By cooling the gas, it is possible to use very efficient quench and scrubbing technology, including wet electrostatic precipitators to ensure a very clean and dry gas for compression for use in engines and gas turbines. The disadvantage of this gas conditioning pathway is that there is a concomitant production of both a solid and liquid stream, that if it cannot be recycled internally in the process, it will have to be treated to ensure its safe disposal in the environment.

Scale Issues: Existing experience with the biomass supply chain shows that sizeable and relatively low-cost feedstock sources are residues from saw mills and furniture manufacturing, along with clean materials that can be taken from the urban and industrial waste streams (such as construction and demolition wood, pallets, and packaging). In most regions, however, this supply would constrain a power plant to a scale of less than 25 MW(e). Significant economies of scale and improvements in generation efficiency can be gained by going to 50 or 75 MW(e) output. Increasing the biomass supply to meet this would require some portion of the feedstock supply to come from dedicated feedstock supply systems such as short rotation forestry or herbaceous energy crops.

Demonstrations: A successful demonstration of a high pressure, LCV gas, biomass integrated gasification and combined cycle (IGCC) was completed in 2000 in the city of Värnamo, Sweden. This first complete biomass-fueled IGCC was constructed by Sydkraft A.B. and is part of the city's district heating system. This facility is fueled with about 18 MW(th) equivalent of wood residues and produces about 6 MW of electricity (4 from the

gas turbine, 2 from the steam cycle) and 9 MW of heat. The gasification system, developed in cooperation between Sydkraft A.B. and Foster Wheeler Energy International, Inc., is a pressurized CFB that is fluidized with air and produces a gas of about $5\div 6 \text{ MJ Nm}^{-3}$ lower heating value. This gas is cooled to $350^{\circ}\text{C} \div 400^{\circ}\text{C}$ before it is cleaned in metal filters and is then passed to the Typhoon gas turbine, which is manufactured by Alstom Company. The project demonstrated more than 1500 hours of IGCC operation on the product gas prior to its shut down at the end of the demonstration phase.

Several atmospheric pressure gasification power systems are under development. As an example, TPS Thermiska Processor A.B. and Kelda Group have constructed the ARBRE power plant in North Yorkshire in the United Kingdom. This atmospheric pressure CFB IGCC is designed to generate 10 MW(e) using SRF (willow) harvested from a 1000 ha plantation as the major feedstock. This system also uses an Alstom Typhoon turbine with a heat recovery steam generator in which extra gas is duct-fired to increase the power output on the steam side, resulting in 4.75 MW(e) from the gas turbine, 5.25 MW(e) from the steam cycle.

There are also MCV gas projects under development in the USA and Europe. Both the *SylvaGas* project, at Future Energy Resources Company (FERCO), and the European Babcock-TUV project are indirect gasification systems based on a moving heat carrier as described above. The *SylvaGas* project is proceeding in multiple phases and is currently operating in a co-firing mode, supplying wood-derived gas to the McNeil biomass station at Burlington Electric of Vermont.

Co-firing is an early development and commercialization pathway for biomass gasification. As a leading example of this, the Foster Wheeler Energia Oy CFB is supplying a LCV gas to an existing large-scale utility boiler at the Kymijärvi 167 MW(e) and 240 MW(th) fossil-fired plant close to the Finnish city of Lahti. The Foster Wheeler plant has been operating for several years. The fuel used is a combination of forestry residues, industrial wood residues, and recycled fuel (a clean fraction of the municipal waste stream composed mainly of wood, paper, and cardboard, which is separated at source). This project builds on many years of successful operation of biomass CFBs in thermal applications and substitutes for about 15% of the total fuel used in the boiler.

Small-scale gasifiers for the production of fuel gas for cooking, and the demonstration of electricity in ICEs are already commercial in both India and China. The introduction of these technologies has been accelerated by the use of moderate government subsidies, especially for communities that are not served by the electricity grid. In development circles such systems are often referred to village power systems. There is considerable discussion among the OECD nations about the use of distributed energy resources, which would provide local power and heat (they are often CHP units) while remaining connected to the grid. Many of these units are based on natural gas; however, where the economics and availability of biomass is appropriate, gasification is considered and there are demonstrations of gasifier-ICE with CHP applications in district heating in Denmark.

Economics and Commercialization: The widespread demonstration of biomass-fueled advanced gasification cycles shows the increased emphasis on efficiency and economics that this carbon neutral technology is attracting. The economics of the first demonstration

systems are such that they all enjoy some level of government investment support. However, investment costs are expected to decline from today's 1800 \$ kW⁻¹ to 1100÷1300 \$ kW⁻¹ for the Nth plants at scales above 50 MW(e). The integrated demonstrations evaluate many of the environmental and social benefits that these technologies will provide for rural and economic development in many areas of the world. Early markets for the technology are foreseen to be in the biomass processing industries in CHP applications, which will effectively double the electricity-to-heat ratio of today's steam cycle systems.

4.4 Liquid Fuels and Chemicals Production

The conversion of the gas output from biomass gasification to a clean syngas, composed of hydrogen and carbon monoxide, would enable the production of liquid fuels and chemicals such as ammonia and hydrogen by well established and proven syngas technologies. Today these processes utilize the syngas produced by the steam reforming of natural gas or use syngas from coal gasification.

The production of liquid fuels from syngas has a long history, which goes back to the pioneering work of Fisher and Tropsch to synthesize hydrocarbon fuels in Germany in the 1920s. The process was implemented in Germany in the 1930s. Nine plants operated during WWII on syngas from coal gasification; and after the war, until the mid 1950s, they operated on syngas from the gasification of heavy oil. In the 1950s, South Africa constructed the first of the South African Synthetic Oil Limited (SASOL) plants, an activity that has continued its development to the present day using syngas produced from both coal and natural gas. Both of these developments were initiated, during times of petroleum shortages, to fuel the transportation systems of Germany and South Africa. Continuing research and development is based on the environmental advantages of producing zero sulfur fuels, with properties tailored to specific engines to minimize emissions from petroleum-derived fuels. At the time of writing, there are at least six developers of what are known as Fischer-Tropsch Liquids (FTL) plants, which are scaled to use remote and difficult to get to market sources of natural gas as the feedstock for the syngas.

Other syngas processes can be optimized to produce alcohols and ethers as fuels or chemicals; these are described below.

4.4.1 Fischer-Tropsch Production of Hydrocarbon Liquid Fuels

FTL processes use catalysts based mainly on Iron, Cobalt, Ruthenium, and Potassium, and have been extensively characterized. They operate at high pressures between 2.5 and 4.5 MPa, and temperatures between 220°C and 450°C. The reactors range from fixed catalyst beds to both bubbling and circulating fluidized beds. The product distribution depends on the polymerization on the surface of the catalyst. The hydrocarbon chains are built up - one carbon atom at a time, a process known as homologation. Polymer growth of this type is now understood to take place via what is known as the Anderson-Shulz-Flory mechanism, and it is not possible to produce either a single compound with a fixed number of carbon atoms or even a narrowly defined distribution of molecular weights. Extensive product recycling and recirculation of unreacted syngas can be used to reduce the number of small hydrocarbon molecules (e.g., C₁ - C₅); however, there is also a production of wax-like molecules with as many as 30 to 50 carbon atoms. The conversion per pass of the syngas

over the catalysts is often limited, due in part to the fact that the polymerization reaction is exothermic and the equilibrium mixtures obtained are very temperature sensitive, affecting the yield and proportions of the desired products. The recycle processes are very energy intensive and reduce the throughput of the catalyst system.

Recent progress in enhancing the yields of gasoline and diesel products has been made partly by optimization of the catalysts and operating conditions, and also by companies such as Shell with its Shell Middle Distillate Synthesis (SMDS) process in which the higher molecular weight waxes are hydrotreated over selective catalysts to increase the yield of the desired range of hydrocarbons C_8 through C_{20} . The smaller carbon number products, $C_1 - C_5$, are also reformed to increase the hydrogen to the overall process.

Other innovations in the FTL arena include slurry reactors, which use very finely divided catalysts suspended in an oil medium. Such reactors often demonstrate much increased conversion in a single pass and offer economies with respect to recycle energy and investment. However, from the chemical engineering perspective, such three-phase reaction systems have required a lot of R&D and development.

An alternative production process would use a high conversion single pass catalyst such as a slurry reactor and then utilize the tail gas after the catalyst as fuel for a gas turbine combined cycle. Such a process would then co-produce electricity, heat, and a liquid fuel, and offer lower investment costs and higher overall efficiency.

4.4.2. The production of Methanol and Higher Alcohols from Syngas

Methanol, unlike ethanol, is rarely used as a heat fuel or as a blend with gasoline. It is, however, widely used as a component of methyl tertiary-butyl ether (MTBE), which is a high octane oxygenate that is added to gasolines to provide up to 2.7% oxygen in the final fuel to meet Clean Air Act regulations in the USA. Unlike ethanol it is not possible to use methanol in blends with gasoline in Northern countries because it results in a phase separation, into a water-methanol layer and a gasoline layer that cannot be utilized in engines. Methanol synthesis over copper-based catalysts has developed to the point where the process is both highly selective and efficient. The remaining challenge is the issue of syngas conversion to methanol per pass over the catalyst. Liquid phase methanol synthesis in a slurry offers higher rates of conversion and better management of the heat generated.

Higher alcohols are produced from syngas over typical Fischer-Tropsch catalysts under conditions of greater severity than those used in the production of predominantly hydrocarbons. Pressures are between 5 and 15 MPa and are generally at temperatures higher than FTL synthesis. The Anderson-Shulz-Flory mechanism does not appear to determine the product distribution, though homologation through the addition of one carbon atom at a time is followed, so that product methanol is recycled over the catalyst to grow into higher alcohols. Changes in catalyst composition can determine the isomer composition of the higher ($> C_3$) alcohols.

Biological synthesis of ethanol is also possible using an anaerobic bacterium, *Clostridium ljungdahlii*. Though not yet commercialized, many of the development challenges of producing the bacterium and making effective gas liquid contactors and bioreactors have

been overcome. Yields are similar to those from the inorganic high temperature Fischer-Tropsch catalysts.

4.4.3. DiMethyl Ether and Gasolines from Methanol

DiMethyl Ether (DME) has been of interest to a number of fuels developers as it has similar properties to propane. A gas at room temperature, its critical point parameters are 400K and 5.3 MPa, while that of propane are 370K and 4.21 MPa. DME would be transported as a liquid and could be distributed in bottles for cooking in developing countries and as a good diesel fuel replacement (similar to distribution of liquefied petroleum gas). It also is quite reactive chemically and could be used as a building block to prepare higher ethers, MTBE, and methyl acetate. Its production from methanol is by means of dehydration; however, by using mixed methanol synthesis catalysts and a dehydration catalyst such as alumina, DME is produced in high yield and conversion per pass from syngas, at much lower pressures of 5 MPa (reduced capital investment) than straight methanol synthesis. In the 1990s a methanol-to-gasoline (MTG) process was operated at a commercial scale in New Zealand, using the natural gas as the steam reforming feedstock.

5. Conclusions

The use of thermochemical processing, based on pyrolysis and gasification of biomass to produce solid, liquid, and gaseous fuels is an area of considerable development, offering high efficiency and good environmental performance characteristics. Advanced pyrolysis processes are already commercial and can be used to manufacture chemical intermediates as well as a fuel to replace oil in combustion systems. Gasification at both large and small scales is being adopted for electricity and heat generation. Gasification also offers a route to liquid fuels and eventually hydrogen to address the severe transportation fuel supply challenge that is developing.

All of these developments have relied on advances in the science and technology of biomass processing as well as the developments in materials process control technologies to make fuels and products that are competitive in cost and performance with traditional hydrocarbon sources.

Glossary

BFB:	Bubbling fluidized bed
CFB:	Circulating fluidized bed
CHP:	Combined heat and power
DME:	DiMethyl Ether
Dp:	Degree of polymerization
EH&S:	Environment, Health, and Safety
FTL:	Fischer-Tropsch Liquids
HHV:	Higher heating value
ICE:	Internal combustion engine
IGCC:	Integrated gasification and combined cycle

LCV:	Low calorific value
LHV:	Lower heating value
MCV:	Medium calorific value
MTBE:	Methyl tertiary-butyl ether
NREL:	National Renewable Energy Laboratory (USA)

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Biographical Sketch

Ralph P. Overend, NREL Research Fellow, was trained in physical chemistry, and worked in bioenergy and renewable energy since 1973 as a researcher, research manager, and coordinator of research and development in both Canada and the United States. His nearly 20 years with the National Research Council of Canada, was as manager of the Bioenergy program, and advisor to the Department of Energy Mines and Resources on biomass energy. In addition, he served as coordinator of Canadian renewables R&D for several years. He joined the United States Department of Energy Biomass Power program at the National Renewable Energy Laboratory in 1990, and has worked extensively in the development of long-range plans and strategies for biomass power and biofuels since that time. His major technical activity at the present time is assisting the development of the Vermont Gasification project—a 60 MW thermal indirect gasification system attached to the McNeil station in Burlington, Vermont.

He was the Chairman of the American Chemical Society Cellulose Division 1993-94. He edits the journal, *Biomass and Bioenergy*, and the biomass section of the Journal, *Solar Energy*, in addition to being a member of several editorial boards. He has also served as a United Nations, World Bank, and FAO lecturer/advisor in the USSR, China, Pakistan, and Mexico. He recently completed the biomass component of a renewable energy atlas for the Government of the Philippines.

Significant recognitions for outstanding scientific contributions in biomass and bioenergy include: Fellow of the Chemical Institute of Canada, 1990; Johannes Linneborn Prize, 1996; H.M. Hubbard Award, 1997; R&D 100 Award, 1998; NREL Research Fellow, 2000; the Thomas R. Miles Award, 2001, and the World Renewable Energy Network, Pioneer Award, 2002.

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SAMPLE CHAPTER