

# Chapter 2

## Green Energy Facilities

### 2.1 Introduction

Modern bioenergy involves commercial energy production from biomass for industry, power generation, or transport fuels. Bioenergy is an all-inclusive term for all forms of biomass and biofuels. Green energy is an alternate term for renewable energy used to indicate that the energy is generated from sources considered environmentally friendly. Various biomasses such as wood, straw, and even household wastes may be economically converted into bioethanol. Bioethanol is derived from the alcoholic fermentation of sucrose or simple sugars, which are produced from biomass by a hydrolysis process. Biodiesel is an environmentally friendly alternative liquid fuel that can be used in any diesel engine without modification.

The importance of biomass in different world regions is given in Table 2.1. For large portions of the rural populations of developing countries, and for the poorest sections of urban populations, biomass is often the only available and affordable

**Table 2.1** Importance of biomass in different world regions

Region	Share of biomass in final energy consumption
Africa (average)	62.0
Burundi	93.8
Ethiopia	85.6
Kenya	69.6
Somalia	86.5
Sudan	83.7
Uganda	94.6
South Asia (average)	56.3
East Asia (average)	25.1
China	23.5
Latin America (average)	18.2
Europe (average)	03.5
North America (average)	02.7
Middle East (average)	0.3

source of energy for basic needs such as cooking and heating. As shown in Table 2.1, the importance of biomass varies significantly across regions. In Europe, North America, and the Middle East, the share of biomass averages 2 to 3% of total final energy consumption, whereas in Africa, Asia, and Latin America, which together account for three-quarters of the world's population, biomass provides a substantial share of the energy needs: a third on average, but as much as 80 to 90% in some of the poorest countries of Africa and Asia (e.g., Angola, Ethiopia, Mozambique, Tanzania, Democratic Republic of Congo, Nepal, and Myanmar).

Traditional biomass markets have been inefficient, but technological developments have reduced energy, emissions, and material flows through the system thus improving the efficiency of biomass energy systems. The energy market demands cost effectiveness, high efficiency, and reduced risk to future emission limits. Modern biomass conversion technologies offer (a) the potential for high yields, (b) economic fuel availability, (c) low adverse environmental impacts, and (d) suitability to modern energy systems. A number of systems that meet the aforementioned criteria for modernized biomass conversion can be identified (Larson 1993).

## 2.2 Biomass Feedstocks

The term biomass (Greek *bio*, life + *maza* or mass) refers to nonfossilized and biodegradable organic material originating from plants, animals, and microorganisms derived from biological sources. Biomass includes products, byproducts, residues and waste from agriculture, forestry, and related industries as well as the nonfossilized and biodegradable organic fractions of industrial and municipal solid wastes. The term biomass refers to wood, short-rotation woody crops, agricultural wastes, short-rotation herbaceous species, wood wastes, bagasse, industrial residues, waste paper, municipal solid waste, sawdust, biosolids, grass, waste from food processing, aquatic plants and algae animal wastes, and a host of other materials.

Biomass is organic material that has stored sunlight in the form of chemical energy. It is commonly recognized as an important renewable energy; during the growth of plants and trees, solar energy is stored as chemical energy via photosynthesis, which can be released via direct or indirect combustion.

Biomass is very important for implementing the Kyoto agreement to reduce carbon dioxide emissions by replacing fossil fuels. Surging energy requirements in parallel with technological developments have forced research and development activities to focus on new and biorenewable energy.

There are three ways to use biomass. It can be burned to produce heat and electricity, changed to gaslike fuels such as methane, hydrogen, and carbon monoxide, or changed to a liquid fuel. Liquid fuels, also called biofuels, include mainly two forms of alcohol: ethanol and methanol. Because biomass can be converted directly into a liquid fuel, it could some day supply much of our transportation fuel needs for cars, trucks, buses, airplanes, and trains. This is very important because nearly one-third of our nation's energy is now used for transportation.

Biomass feedstocks are marked by their tremendous diversity, which makes them rather difficult to characterize as a whole. Feedstocks that can be utilized with conversion processes are primarily the organic materials now being landfilled. These include forest product wastes, agricultural residues, organic fractions of municipal solid wastes, paper, cardboard, plastic, food waste, green waste, and other waste. Nonbiodegradable organic feedstocks, such as most plastics, are not convertible by biochemical processes. Biobased materials require pretreatment by chemical, physical, or biological means to open up the structure of the biomass. The general categories of biomass feedstock are shown in Table 2.2.

**Table 2.2** Major categories of biomass feedstocks

Forest products	Wood; logging residues; trees, shrubs, and wood residues; sawdust, bark, etc.
Biorenewable wastes	Agricultural wastes, crop residues, mill wood wastes, urban wood wastes, urban organic wastes
Energy crops	Short-rotation woody crops, herbaceous woody crops, grasses, starch crops, sugar crops, forage crops, oilseed crops, switchgrass, miscanthus
Aquatic plants	Algae, Water weed, water hyacinth, reed and rushes
Food crops	Grains, oil crops
Sugar crops	Sugar cane, sugar beets, molasses, sorghum
Landfill	Hazardous waste, nonhazardous waste, inert waste, liquid waste
Organic wastes	Municipal solid waste, industrial organic wastes, municipal sewage and sludges
Algae	Prokaryotic algae, eukaryotic algae, kelps
Mosses	Bryophyta, polytrichales
Lichens	Crustose lichens, foliose lichens, fruticose lichen

## 2.3 Green Energy

Green energy is an alternate term for renewable energy used to indicate that the energy is generated from sources considered environmentally friendly (e.g., hydro, solar, biomass, or wind). Green power is sometimes used in reference to electricity generated from “green” sources. Green energy production is the principal contributor to the economic development of developing countries, whose economic development is based on agricultural production and where most people live in rural areas. Implementation of integrated community development programs is therefore very necessary.

Green power refers to electricity supplied from energy sources that are more readily renewable than traditional electrical power sources. Green power products, which can be derived from renewable energy sources, have become widespread in many electricity markets worldwide. The environmental advantages of green electricity seem clear. Market research indicates that there is a large potential market for green energy in Europe generally. Green power marketing has emerged in more than a dozen countries around the world.

Many green electricity products are based on renewable energy sources like wind, biomass, hydro, biogas, solar, and geothermal (Murphy and Niituma 1999). There has been interest in electricity from renewable sources known as green electricity or green pools as a special market (Elliott 1999). The term green energy is also used to describe green energy produced from cogeneration, energy from municipal waste, natural gas, and even conventional energy sources. The use of green energy sources like hydro, biomass, geothermal, and wind energy in electricity production reduces CO<sub>2</sub> emissions (Fridleifsson 2003). Emissions such as SO<sub>2</sub>, CO<sub>2</sub>, and NO<sub>x</sub> are reduced considerably and the production and use of green electricity contributes to diminishing the greenhouse effect (Arkesteijn and Oerlemans 2005).

In general, a sustainable energy system includes energy efficiency, energy reliability, energy flexibility, energy development and continuity, combined heat and power (CHP) or cogeneration, fuel poverty, and environmental impacts. The environmental impacts of energy use are not new. For centuries, wood burning has contributed to the deforestation of many areas. On the other hand, the typical characteristics of a sustainable energy system can be derived from political definitions. A sustainable energy system can be defined also by comparing the performance of different energy systems in terms of sustainability indicators (Alanne and Sari 2006). Because, by definition, sustainable energy systems must support both human and ecosystem health over the long term, goals on tolerable emissions should look well into the future. They should also take into account the public's tendency to demand more (UNDP 2000).

## 2.4 Importance of Biomass

Biomass is organic material that has stored sunlight in the form of chemical energy. It is a general term for material derived from growing plants or from animal manure. Biomass includes wood and logging residues, agricultural crops and their waste byproducts, the organic portion of municipal solid waste, animal wastes, municipal biosolids (sewage), waste from food processing, and aquatic plants and algae (Hall *et al.* 1993). All biomass is produced by green plants converting sunlight into plant material through photosynthesis. Photosynthesis is a carbon fixation reaction achieved by the reduction of carbon dioxide. The fixation or reduction of carbon dioxide is a light-independent process. Although some of the steps in photosynthesis are still not completely understood, the overall photosynthetic equation has been known since the 1800s.

Biomass appears to be an attractive feedstock for three main reasons. First, it is a renewable resource that could be sustainably developed in the future. Second, it appears to have considerable environmentally friendly properties, resulting in no net releases of carbon dioxide and very low sulfur content. Third, it appears to have significant economic potential provided that fossil fuel prices increase in the future.

Agricultural residues such as straws, nut shells, fruit shells, fruit seeds, plant stalks and stovers, green leaves and molasses are potential renewable energy sources.

Current disposal methods for these agricultural residues have caused widespread environmental concerns. For example, disposal of rice and wheat straw by open-field burning causes air pollution (Zhang and Zhang 1999).

Agricultural energy or green energy production is the principal contributor to the economic development of a developing country, whose economic development is based on agricultural production, and most people live in rural areas. Implementation of integrated community development programs is therefore very necessary. It is believed that integrated community development promotes the socioeconomic advancement of developing countries.

The biomass produced in Brazil results largely from an ethanol fuel production program started in 1975 from sugar cane crops grown specifically for fuel use, presently occupying 2.7 million hectares of land and employing about 350 distilleries. Ethanol currently provides over 40% of the fuel consumed by cars and light trucks. It is estimated to have saved Brazil over \$40 billion in oil imports, excluding the costs of the program. In 1999, carbon emissions were reduced by almost 13 megatons as a result of the program, and local emissions of lead, sulfur, and carbon monoxide have been greatly reduced. In addition, according to the United Nations Development Programme, ethanol production supports about 700,000 rural jobs (UNDP 2000).

Biomass has historically been a dispersed, labor-intensive, and land-intensive source of energy. Therefore, as industrial activity has increased in countries, more concentrated and convenient sources of energy have been substituted for biomass. Selection of a particular biomass for energy requirements is influenced by its availability, source and transportation costs, competing uses, and prevalent fossil fuel prices.

Biomass provides a clean, renewable energy source that could dramatically improve our environment, economy, and energy security. Biomass energy generates far less air emissions than fossil fuels, reduces the amount of waste sent to landfills, and decreases our reliance on foreign oil. Biomass energy also creates thousands of jobs and helps revitalize rural communities.

Energy can be obtained from direct combustion of biomass by burning of dry organic matter, such as woody scraps, grasses, and agricultural residues. Biomass can be thermochemically converted into liquid fuel and into gases, such as methane, carbon monoxide, or hydrogen, by pyrolysis. Bioethanol can be obtained from cellulosic biomass by fermenting and distilling sugar solutions. Vegetable oils such as soybean and canola oils can be chemically converted into liquid fuel known as biodiesel. These fuels can be used as diesel fuel and gasoline in conventional engines with little modification to the system. Certain organic compounds, specifically municipal biosolids (sewage) and animal wastes (manures), can be biochemically converted into methane by anaerobic digestion.

Certain transportation biofuels such as bioethanol, biodiesel, methyltetrahydrofuran, and dimethyl ether can be sustainably obtained from biomass. Biofuels can be used in pure form or blended with gasoline.

In industrialized countries, the main biomass processes utilized in the future are expected to be the direct combustion of residues and wastes for electricity gener-

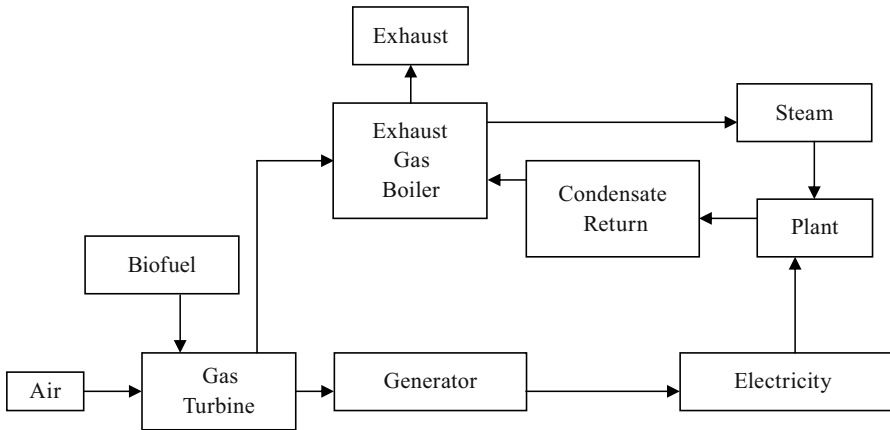
ation, bioethanol and biodiesel as liquid fuels, and combined heat and power production from energy crops. The electricity is produced by the direct combustion of biomass and by advanced gasification and pyrolysis technologies that are almost ready for commercial-scale use.

Bioenergy, the energy from biomass, has been used for thousands of years, ever since people started burning wood to cook food or to keep warm, and today wood is still our largest biomass resource for bioenergy. Many countries in the developing world still use wood as their primary fuel (Demirbas and Demirbas 2007). In the future, biomass has the potential to provide a cost-effective and sustainable supply of energy, while at the same time aiding countries in meeting their greenhouse-gas-reduction targets. In the short to medium term, biomass is expected to dominate energy supply. For the generation of electricity and heat, with the use of advanced combustion technology, organic wastes can be used as biomass. Also a number of crops and crop residues may fit modern bioenergy chains (Pimentel *et al.* 1981; Haberl and Geissler 2000; Hoogwijk *et al.* 2003). Biomass is the most common form of carbonaceous materials, which are widely used in the third world.

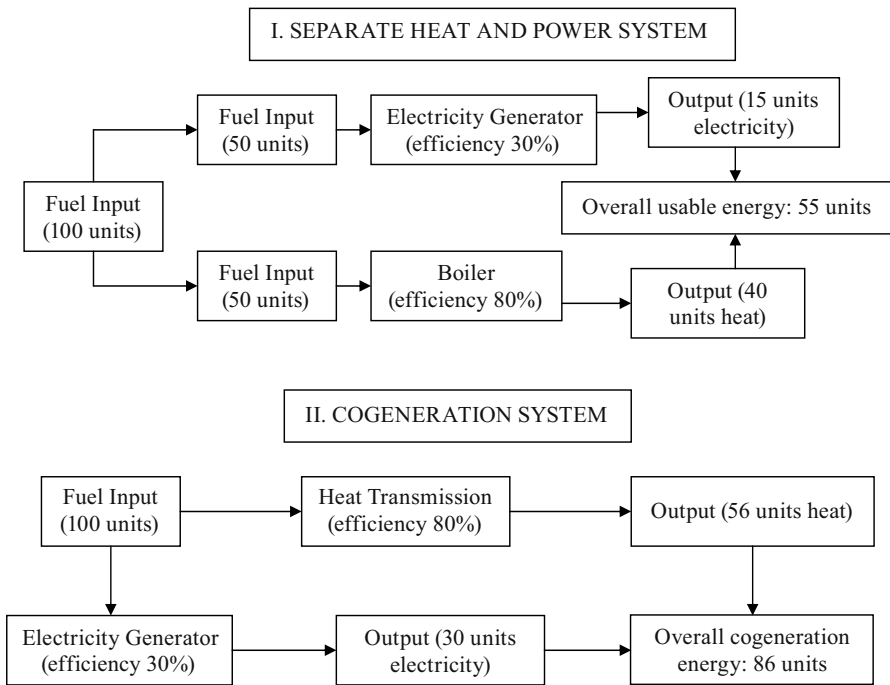
Biomass gasification technologies make it possible to convert renewable biomass materials into clean fuel gases or synthetic gases. These gaseous products can be burned to generate heat or electricity, or they can potentially be used in the synthesis of liquid transportation fuels, hydrogen, or chemicals. Gasification offers a combination of flexibility, efficiency, and environmental acceptability that is essential in meeting future energy requirements. Biomass-fueled renewable distributed generation technologies in rural electrification provide no-regret options with significant CO<sub>2</sub> emission mitigation potential when operated under a net-metering scheme (Karki *et al.* 2008).

Cogeneration, in and of itself, is an example of pollution prevention. Cogenerators, by using excess heat, may enhance the efficiency of total energy use by up to 80% or more from the typical 33 to 38% efficiency of electricity-only generation. A typical cogeneration system consists of an engine, steam turbine, or combustion turbine that drives an electrical generator. Figure 2.1 shows a gas turbine topping cycle cogeneration system. The figure is a diagram of a gas turbine of the type used in cogeneration power plants ranging in size from about 500 kW to 50 MW. These turbines are similar to jet engines used in aircraft. In this size range, gas turbines are more efficient than any other type of fossil-fuel-fired power plants, reaching electrical efficiencies of up to 45% or even, with the addition of waste heat recovery (cogeneration), efficiencies of over 80%. When used for cogeneration, the hot exhaust gases from the gas turbine are passed through a heat exchanger where the heat is transferred to water in pipes producing steam. A waste heat exchanger recovers waste heat from the engine or exhaust gas to produce hot water or steam. Cogeneration produces a given amount of electric power and process heat with 15 to 35% less fuel than it takes to produce the electricity and process heat separately (Demirbas 2006c).

Figure 2.2 illustrates a comparison between energy inputs to separate and cogenerative generation systems. Traditional coal-, oil-, or natural-gas-fired thermal generating stations convert only about one-third of the initial energy contained within



**Figure 2.1** A representative cogeneration: a gas turbine topping cycle



**Figure 2.2** Comparison between energy inputs to separate heat and power system and cogeneration system

the fuel into useful electricity. The remainder of the energy is discarded as heat without serving any useful purpose. From 10 to 35% of primary energy use is wasted as conversion losses in power plants. Cogeneration can increase the efficiency of

a fossil fuel from an average of 40 to over 80%. Figure 2.2 illustrates the increase in efficiency. This increase in efficiency can translate into lower costs and fewer emissions of pollutants than the conventional alternative of generating electricity and heat separately (Demirbas 2006c).

## 2.5 Production of Fuels and Chemicals from Biomass

Biomass provides a potential source of added value chemicals, such as reducing sugars, furfural, ethanol, and other products, by using biochemical or chemical and thermochemical processes. The gas phase of pyrolytic degradation products contains mostly carbon monoxide and carbon dioxide and minor proportions of hydrogen, methane, ethane, and propane. The liquid fraction consists mainly of water, with small proportions of acetaldehyde, propion aldehyde, butiraldehyde, acrolein, crotonaldehyde, furan, acetone, butanedione, and methanol. The sugars from the hemicelluloses are also fermented into bioethanol.

More recently, many attempts have been made to utilize biomass, such as wood, hazelnut shell, agricultural waste residues, waste paper and wheat straw, tea waste, and olive husk. The main biomass sources in use for energy production range from forest residues, agricultural residues, pulp and paper operation residues, animal waste, and landfill gas to energy crops.

Gasification followed by Fischer–Tropsch synthesis (FTS) is currently the most promising method for upgrading low-value coal and biomass to high-value liquid fuels and chemicals. The total biomass produced each year as waste material from agriculture and forest operations could be converted into roughly 40 billion gal/year of liquid fuels (roughly 25% of the current US gasoline usage).

Tijmensen *et al.* (2002) review the technical feasibility and economics of a biomass integrated gasification Fischer–Tropsch (BIG-FT) process and also point out the key R&D issues involved in the commercialization of this process. Boerrigter and den Uil (2002) give a similar review identifying a potential BIG-FT process configuration. The FTS for the production of liquid hydrocarbons from coal-based synthesis gas has been the subject of renewed interest for the conversion of coal and natural gas into liquid fuels (Jin and Datye 2000).

To produce biosyngas from a biomass fuel, the following procedures are necessary: (a) gasification of the biomass, (b) cleaning of the product gas, and (c) use of the synthesis gas to produce liquid fuel via FTS.

Hydrothermal liquefaction (HTL) or direct liquefaction is a promising technology to treat waste streams from various sources and produce valuable bioproducts such as biocrudes. A major problem with commercializing HTL processes for biomass conversion today is that it remains uneconomical when compared to the costs of diesel or gasoline production. High transportation costs of large quantities of biomass increase production costs, and a poor conversion efficiency, coupled with a lack of understanding of complex reaction mechanisms, inhibits the widespread commercial use of the process.



In the HTU process, biomass is reacted in liquid water at elevated temperature and pressure. The phase equilibria in the HTU process are very complicated due to the presence of water, supercritical carbon dioxide, alcohols, and so-called biocrude. Biocrude is a mixture with a wide molecular weight distribution and consists of various kinds of molecules. Biocrude contains 10 to 13% oxygen and is upgraded by catalytic hydrodeoxygenation in a central facility. Preliminary process studies on the conversion of various biomass types into liquid fuels have indicated that HTU is more attractive than pyrolysis or gasification. In HTU the biomass, typically in a 25% slurry in water, is treated at temperatures of 575 to 700 K and 12 to 18 MPa pressures in the presence of liquid water for 5 to 20 min to yield a mixture of liquid biocrude, gas (mainly CO<sub>2</sub>), and water. Subsequent processing may be able to upgrade the biocrude to useable biofuel. A large proportion of the oxygen is removed as carbon dioxide (Goudriaan and Peferoen 1990).

Biomass, such as wood, with a lower energy density is converted into biocrude with a higher energy density, organic compounds, mainly alcohols and acids, and gases, mainly CO<sub>2</sub>. Water is also a byproduct. In the products, CO<sub>2</sub>, the main component of the gas product, can be used to represent all gas produced, and methanol and ethanol represent organic compounds. The feedstocks, reaction conditions, and products for the HTU process are given in Table 2.3. In Table 2.3, the weight fraction of each component is assigned on the basis of the data of the vacuum flash of biocrude and the data of a pilot plant (Feng *et al.* 2004).

**Table 2.3** Representatives for the products from the HTU process

Product	Component	Weight fraction (%)
Biocrude	Polycarbonates	47.5
	Methyl- <i>n</i> -propyl ether	2.5
Gas	Carbon dioxide	25.0
Organic compounds	Methanol	5.0
	Ethanol	3.5
Water	Water	16.5

One of the first HTL studies was conducted by Kranich (1984) using municipal waste materials (MWMs) as a source to produce oil. Three different types of materials from an MSW plant were used: primary sewage sludge, settled digester sludge, and digester effluent. Using a magnetically stirred batch autoclave with a hydrogen feed system, slurry feed device, a pressure and temperature recorder, and a wet-test meter for measuring gas product, Kranich processed the waste sources. The feedstock was first dried and then powdered. The wastes were also separated into different oil and water slurries and processed separately. Temperatures ranged from 570 to 720 K with pressures of up to 14 MPa. Retention times also varied between 20 and 90 min. Hydrogen was used as the reducing gas with initial pressures of up to 8.3 MPa. Three types of catalyst were studied: sodium carbonate, nickel carbonate, and sodium molybdate. The slurry feedstock was injected into the reactor through

a pressurized injector and the oil product was extracted by pentane and toluene. Results showed that organic conversion rates varied from 45 to 99% and oil production rates were reported from 35.0 to 63.3%. Gas products were found to contain H<sub>2</sub>, CO<sub>2</sub>, and C<sub>1</sub>–C<sub>4</sub> hydrocarbons.

The experimental results showed no significant differences between the applications of the three different catalysts. Kranich recommended that the water slurry system was not feasible for scale-up, and considerations of a commercial scale process were confined to only the oil slurry system. It was also concluded that no further development work on hydroliquefaction of sewage sludge to oil was necessary. Kranich's recommendation did not hold, mainly due to increases in crude oil prices and the need to find new technologies for energy procurement, and thus many studies on liquefaction of sewage sludge have since been conducted. Research has indicated that liquefaction is a feasible method for the treatment of sewage sludge wastes and has a high oil-producing potential (Suzuki *et al.* 1986; Itoh *et al.* 1994; Inoue *et al.* 1997). Today HTL research is still being conducted with sewage sludge; however, focus has shifted to include many varieties of biomass materials. Table 2.4 shows feedstocks, reaction conditions, and the products for the HTU process.

Several technologies have been developed to convert biomass into a liquid biofuel with a higher heating value, such as gasification, fast pyrolysis, and HTU. In the HTU, the biomass is treated for 5 to 20 min with water under subcritical conditions (575 to 625 K, 10 to 18 MPa) to give a heavy organic liquid (biocrude) with a heating value of 30 to 35 MJ/kg. During this process, the oxygen content of the organic material is reduced from about 40% to between 10 and 15%. The removed oxygen ends up in CO<sub>2</sub>, H<sub>2</sub>O, and CO. After 1.6 s at 595 K and 25 MPa, 47% conversion of

**Table 2.4** Feedstocks, reaction conditions, and products for HTU process

Biomass feedstocks	Wood and forest wastes Agricultural and domestic residues Municipal solid wastes Organic industrial residues Sewage sludge
Reaction conditions	Temperature: 575–625 K Pressure: 12–18 MPa Resistance time: 5–20 min Medium: Liquid water
Main chemical reactions	Depolymerization Decarboxylation Dehydration Oxygen removed as CO <sub>2</sub> and H <sub>2</sub> O Hydrodeoxygenation Hydrogenation
Products (%wt. on feedstock)	Biocrude: 45 Water-soluble organics: 10 Gas (> 90% CO <sub>2</sub> ): 25 Process water: 20
Thermal efficiency	70–90%

cellulose in water was obtained yielding hydrolysis products (cellobiose, glucose, etc., 44%) and decomposition products of glucose (erythrose, 1,6-anhydroglucose, 5-hydroxymethylfurfural, 3%). Furthermore, it has been shown that cellobiose decomposes via hydrolysis into glucose and via pyrolysis into glycosylerythrose and glycosylglycolaldehyde, which are further hydrolyzed into glucose, erythrose, and glycolaldehyde. Hydrolysis refers to the splitting up of organic particles into smaller organic fragments in water. Hydrothermal decomposition also acts on large organic molecules, reducing them into smaller fragments, some of which dissolve in water.

In the HTU process, biomass chips are pressurized and digested at 575 to 700 K with recycled water from the process. Subsequently the digested mass is pressurized to 12 to 18 MPa and reacted in liquid water at 575 to 700 K for 5 to 15 min. Under these conditions decarboxylation and depolymerization take place and a biocrude is formed that separates from the water phase. Part of the process water is recycled. Obviously, the process is very simple with high efficiency.

Hydrothermal reaction involves applying heat under pressure to achieve a reaction in an aqueous medium. The treatment of organic wastes by supercritical water (SCW) reaction occurs in a homogeneous phase where interface mass transfer limitations are avoided and reaction efficiencies of 99.9% can be achieved at residence times of less than 1 min. Because of the distinctive characteristics of water described above, hydrothermal reactions are an effective method for the treatment of organic wastes. The reactions can be performed under sub- or supercritical conditions. They can also be classified into two broad categories: (a) oxidative, i.e., involving the use of oxidants, and (b) nonoxidative, i.e., excluding the use of oxidants.

Pyrolysis oil (bio-oil) from wood is typically a liquid, almost black to dark red brown. The density of the liquid is about  $1,200 \text{ kg/m}^3$ , which is higher than that of fuel oil and significantly higher than that of the original biomass. Bio-oils typically have water contents of 14 to 33 wt%, which cannot be removed by conventional methods like distillation. Phase separation may occur above certain water contents. The higher heating value (HHV) is below 27 MJ/kg (compared to 43 to 46 MJ/kg for conventional fuel oils).

Pyrolysis is the thermal decomposition of organic matter occurring in the absence of oxygen or when significantly less oxygen is present than is required for complete combustion. Pyrolysis is the basic thermochemical process for converting biomass into a more useful fuel. Biomass is heated in the absence of oxygen, or partially combusted in a limited oxygen supply, to produce a hydrocarbon-rich gas mixture, an oil-like liquid, and a carbon-rich solid residue. The products of pyrolysis can be gaseous, liquid, or solid. Flash pyrolysis describes the rapid, moderate-temperature (675 to 875 K) pyrolysis that produces liquids. Biomass is heated at rates of 100 to 10,000 K/s, and the vapor residence time is normally less than 2 s. The oil products are maximized at the expense of char and gas. Pyrolysis processes typically use dry biomass sources.

Pyrolysis dates back to ancient Egyptian times, where tar for caulking boats and an embalming agent were made from pyrolysis. In the 1980s, researchers found that the pyrolysis liquid yield could be increased using fast pyrolysis, where a biomass feedstock is heated at a rapid rate and the vapors produced are also condensed

rapidly (Mohan *et al.* 2006). Pyrolysis has been used since the dawn of civilization. If some means is applied to collect the off-gasses (smoke), the process is called wood distillation. The ancient Egyptians practiced wood distillation by collecting tars and pyroligneous acid for use in their embalming industry. Pyrolysis of wood to produce charcoal was a major industry in the 1800s, supplying the fuel for the industrial revolution, until it was replaced by coal. In the late 19th century and early 20th century wood distillation was still profitable for producing soluble tar, pitch, creosote oil, chemicals, and the noncondensable gases often used to heat boilers at the facility. The wood distillation industry declined in the 1930s due to the advent of the petrochemical industry and its lower-priced products.

Pyrolysis is a process similar to gasification except that it is generally optimized for the production of fuel liquids (pyrolysis oils) that can be used straight or refined for higher-quality uses such as engine fuels, chemicals, adhesives, and other products. Pyrolysis and the combustion of pyrolysis-derived fuel liquids and gases also produce the same categories of end products as the direct combustion of solids. Like gasification, their pollution control and conversion efficiencies may be improved.

Pyrolysis and direct liquefaction processes are sometimes confused with each other, and a simplified comparison of the two follows. Both are thermochemical processes in which feedstock organic compounds are converted into liquid products. In the case of liquefaction, feedstock macromolecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst. At the same time, these fragments, which are unstable and reactive, repolymerize into oily compounds having appropriate molecular weights (Demirbas 2006b). With pyrolysis, on the other hand, a catalyst is usually unnecessary, and the light-decomposed fragments are converted into oily compounds through homogeneous reactions in the gas phase. The differences in operating conditions for liquefaction and pyrolysis are shown in Table 2.5.

**Table 2.5** Comparison of liquefaction and pyrolysis

Process	Temperature (K)	Pressure (MPa)	Drying
Liquefaction	525–675	5–20	Unnecessary
Pyrolysis	675–975	0.1–0.5	Necessary

Catalytic cracking is a thermochemical process that employs catalysts using hydrogen-driven reducing reactions to accelerate the breakdown of high molecular weight compounds (e.g., plastics) into smaller products for the purposes of improving selectivity and imparting certain desirable characteristics to the final product, such as volatility and flashpoint of liquid fuels. This cracking process is often employed in oil refinery operations to produce lower molecular weight hydrocarbon fuels from waste feedstocks. These include gasoline from heavier oils, distillation residuals, and waste plastic.

In wood derived pyrolysis oil, specific oxygenated compounds are present in relatively large amounts. A current comprehensive review focuses on the recent de-

velopments in the wood/biomass pyrolysis and reports the characteristics of the resulting bio-oils, which are the main products of fast wood pyrolysis (Mohan *et al.* 2006). Sufficient hydrogen added to the synthesis gas to convert all of the biomass carbon into methanol carbon would more than double the methanol produced from the same biomass base.

Rapid heating and rapid quenching produced the intermediate pyrolysis liquid products, which condense before further reactions break down higher-molecular-weight species into gaseous products. High reaction rates minimize char formation. Under some conditions, no char is formed. At higher fast pyrolysis temperatures, the major product is gas. Many researchers have attempted to exploit the complex degradation mechanisms by conducting pyrolysis in unusual environments (Mohan *et al.* 2006). The main pyrolysis variants are listed in Table 2.6.

**Table 2.6** Pyrolysis methods and their variants

Method	Residence time	Temperature (K)	Heating rate	Products
Carbonation	Days	675	Very low	Charcoal
Conventional	5–30 min	875	Low	Oil, gas, char
Fast	0.5–5 s	925	Very high	Bio-oil
Flash-liquid <sup>a</sup>	< 1 s	< 925	High	Bio-oil
Flash-gas <sup>b</sup>	< 1 s	< 925	High	Chemicals, gas
Hydropyrolysis <sup>c</sup>	< 10 s	< 775	High	Bio-oil
Methanopyrolysis <sup>d</sup>	< 10 s	> 975	High	Chemicals
Ultra pyrolysis <sup>e</sup>	< 0.5 s	1,275	Very high	Chemicals, gas
Vacuum pyrolysis	2–30 s	675	Medium	Bio-oil

<sup>a</sup> Flash-liquid: liquid obtained from flash pyrolysis accomplished in a time of < 1 s.

<sup>b</sup> Flash-gas: gaseous material obtained from flash pyrolysis within a time of < 1 s.

<sup>c</sup> Hydropyrolysis: pyrolysis with water.

<sup>d</sup> Methanopyrolysis: pyrolysis with methanol.

<sup>e</sup> Ultra pyrolysis: pyrolysis with very high degradation rate.

Main feedstock preparation operations for biomass pyrolysis processes are cleaning, washing, handling, grinding, storing, transporting, and drying. Process variables of biomass pyrolysis are heat flux, temperature, partial pressure, feedstock, particle size, heating rates, residence time, heat and mass transfer, and mineral matter content. Process variables are important. For example, hot-water washing of biomass can improve oil quality and stability for high ash feedstocks. Heating rates, residence time, and heat and mass transfer are affected by particle size.

Activated carbons are carbonaceous materials with a highly developed internal surface area and porosity. Activated carbon is widely used as an effective adsorbent in many applications such as air separation and purification, vehicle exhaust emission control, solvent recovery, and catalyst support because of its high specific pore surface area, adequate pore size distribution, and relatively high mechanical strength. The large surface area results in high capacity for adsorbing chemicals from gases and liquids.

The starting materials used in commercial production of activated carbons are those with high carbon contents such as wood, lignite, peat, and coal of different ranks, or low-cost and abundantly available agricultural byproducts. Activated carbons can be manufactured from virtually any carbonaceous precursor, but the most commonly used materials are wood, coal, and coconut shell. The development of activated carbons from agricultural carbonaceous wastes will be advantageous for environmental problems. In water contamination, wastewater contains many traces of organic compounds, which are a serious environmental problem. In the development of activated carbons, agricultural carbonaceous wastes are used, as this will eliminate the problem of waste disposal while at the same time allowing societies to derive great economic benefits from such commercialized products.

Activated carbons are used in the following applications:

1. They can be used as adsorbents for the removal or reduction of gaseous pollutants from the exhaust gases of industrial sources.
2. They can be used as adsorbents for the removal of volatile organic compounds, ozone from air, mercury and dioxin emissions from incinerator flue gas, and hydrogen sulfide emissions from sewage treatment facilities.
3. They can be used to remove chlorine and organic chemicals (such as phenols, polychlorinated biphenyls, trihalomethanes, pesticides, and halogenated hydrocarbons), heavy metals, and organic contaminants from water.
4. They can be used to extract some harmful elements of cigarette smoke by incorporation in the filter tips of cigarettes.

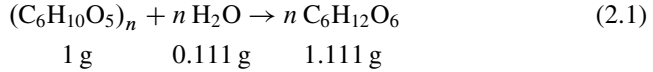
Lignin gives higher yields of charcoal and tar from wood, although lignin has a threefold higher methoxyl content than wood. Phenolics are derived from lignin by cracking the phenyl-propane units of the macromolecule lattice. The formation of char from lignin under mild reaction conditions is a result of the breaking of the relatively weak bonds, like the alkyl-aryl ether bonds, and the consequent formation of more resistant condensed structures, as has already been noted.

Cellulose is a remarkable pure organic polymer consisting solely of units of anhydroglucose held together in a giant straight chain molecule. Cellulose must be hydrolyzed into glucose before fermentation into ethanol. Conversion efficiencies of cellulose into glucose may depend on the extent of chemical and mechanical pretreatments to structurally and chemically alter pulp and paper mill wastes. The method of pulping, the type of wood, and the use of recycled pulp and paper products could also influence the accessibility of cellulose to cellulase enzymes. Hemicelluloses (arabinoglycuronoxylan and galactoglucomannans) are related to plant gums in composition and occur in much shorter molecule chains than cellulose. The hemicelluloses, which are present in deciduous woods chiefly as pentosans and in coniferous woods almost entirely as hexosanes, undergo thermal decomposition very readily. Hemicelluloses are derived mainly from chains of pentose sugars and act as the cement material holding together the cellulose micells and fiber. Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis. Hemicelluloses are largely soluble in alkali and, as such, are more easily hydrolyzed.

Hydrolysis (saccharification) breaks down the hydrogen bonds in the hemicellulose and cellulose fractions into their sugar components: pentoses and hexoses. These sugars can then be fermented into bioethanol.

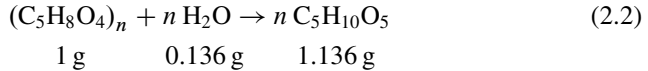
Cellulose [hexosan,  $(C_6H_{10}O_5)_n$ ] hydrolysis produces glucose (a hexose,  $C_6H_{12}O_6$ ). The hydrolysis of cellulose is catalyzed by mineral acids and enzymes.

Hexosan to hexose:



Hemicellulose hydrolysis produces both hexose and pentose sugars – mannose, galactose, xylose, and arabinose – that are not all fermented with existing strains. The hemicelluloses fraction typically produces a mixture of sugars including xylose, arabinose, galactose, and mannose. Both of these are pentosans: xylose and arabinose, and hexosans: galactose and mannose. The hydrolysis of hemicelluloses is catalyzed by mineral acids and enzymes.

Pentosan to pentose:



The most commonly applied methods can be classified into two groups: chemical hydrolysis (dilute and concentrated acid hydrolysis) and enzymatic hydrolysis. In addition, there are other hydrolysis methods in which no chemicals or enzymes are applied. For instance, lignocellulose may be hydrolyzed by gamma-ray or electron-beam irradiation, or by microwave irradiation. However, those processes are commercially unimportant.

Both enzymatic and chemical hydrolyses require a pretreatment to increase the susceptibility of cellulosic materials. In chemical hydrolysis, the pretreatment and the hydrolysis may be carried out in a single step. There are two basic types of acid hydrolysis processes commonly used: dilute acid and concentrated acid, each with variations.

The dilute acid process is conducted under high temperature and pressure and has a reaction time in the range of seconds or minutes, which facilitates continuous processing. As an example, using a dilute acid process with 1% sulfuric acid in a continuous-flow reactor at a residence time of 0.22 min and a temperature of 510 K with pure cellulose provided a yield of over 50% sugars. In this case, 1,000 kg of dry wood would yield about 164 kg of pure ethanol. The combination of acid and high temperature and pressure dictates special reactor materials, which can make the reactor expensive. The first reaction converts the cellulosic materials into sugar and the second reaction converts the sugars into other chemicals. Unfortunately, the conditions that cause the first reaction to occur are also the right conditions for the second to occur.

The biggest advantage of dilute acid processes is their fast rate of reaction, which facilitates continuous processing. Since 5-carbon sugars degrade more rapidly than

6-carbon sugars, one way to decrease sugar degradation is to have a two-stage process. The first stage is conducted under mild process conditions to recover the 5-carbon sugars, while the second stage is conducted under harsher conditions to recover the 6-carbon sugars.

Hydrolysis of cellulosic materials by concentrated sulfuric or hydrochloric acid is a relatively old process. The concentrated acid process uses relatively mild temperatures, and the only pressures involved are those created by pumping materials from vessel to vessel. Reaction times are typically much longer than for dilute acid. This method generally uses concentrated sulfuric acid followed by a dilution with water to dissolve and hydrolyze or convert the substrate into sugar. This process provides a complete and rapid conversion of cellulose to glucose and hemicelluloses into 5-carbon sugars with little degradation. The critical factors needed to make this process economically viable are the optimization of sugar recovery and cost-effective recovery of the acid for recycling. The solid residue from the first stage is dewatered and soaked in a 30 to 40% concentration of sulfuric acid for 1 to 4 h as a precellulose hydrolysis step. The solution is again dewatered and dried, increasing the acid concentration to about 70%. After reacting in another vessel for 1 to 4 h at low temperatures, the contents are separated to recover the sugar and acid. The sugar/acid solution from the second stage is recycled to the first stage to provide the acid for the first stage of hydrolysis.

The primary advantage of the concentrated acid process is the potential for high sugar recovery efficiency. The acid and sugar are separated via ion exchange and then the acid is reconcentrated via multiple effect evaporators. The low temperatures and pressures employed allow the use of relatively low-cost materials such as fiberglass tanks and piping. The low temperatures and pressures also minimize the degradation of sugars. Unfortunately, it is a relatively slow process and cost-effective acid recovery systems have been difficult to develop. Without acid recovery, large quantities of lime must be used to neutralize the acid in the sugar solution. This neutralization leads to the formation of large quantities of calcium sulfate, which requires disposal and creates additional expense.

Another basic method of hydrolysis is enzymatic hydrolysis. Enzymes are naturally occurring plant proteins that cause certain chemical reactions to occur. There are two technological developments important for this process: enzymatic and direct microbial conversion methods.

The chemical pretreatment of the cellulosic biomass is necessary before enzymatic hydrolysis. The first application of enzymatic hydrolysis was used in separate hydrolysis and fermentation steps. Enzymatic hydrolysis is accomplished by cellulolytic enzymes. Different kinds of “cellulases” may be used to cleave the cellulose and hemicelluloses. A mixture of endoglucanases, exoglucanases,  $\beta$ -glucosidases, and cellobiohydrolases is commonly used. The endoglucanases randomly attack cellulose chains to produce polysaccharides of shorter length, whereas exoglucanases attach to the nonreducing ends of these shorter chains and remove cellobiose moieties.  $\beta$ -glucosidases hydrolyze cellobiose and other oligosaccharides to glucose.

For enzymes to work efficiently, they must obtain access to the molecules to be hydrolyzed. This requires some kind of pretreatment process to remove hemicel-



luloses and break down the crystalline structure of the cellulose or removal of the lignin to expose hemicelluloses and cellulose molecules.

The main wood valorization technologies include pulp and paper making, bio-oil by pyrolysis, synthesis gas by gasification, sugar by hydrolysis, ethanol by sugar fermentation, and adhesives by alkali liquefaction and polymerization.

Adhesion is a state in which two surfaces are held together by interfacial forces, which may be valence forces, interlocking action, or both. The adhesives used in commercial wood composite products are usually synthetic polymer resins, based on the condensation reaction of formaldehyde with phenol, urea, resorcinol, or melamine. More than 70% of this urea–formaldehyde resin is used by the forest products industry for a variety of purposes.

The wood adhesive market is very large and problems due to volatile organic compounds and toxic chemicals in many adhesives and their production are significant. In addition, most of the adhesives are derived from depleting petrochemical resources. An environmentally friendly wood adhesive based on renewable resources and produced by microbial fermentation has been explored.

A method is described for making adhesive from biomass. The liquefaction oil is prepared from lignin-bearing plant material and a phenolic fraction is extracted therefrom. The phenolic fraction is reacted with formaldehyde to yield a phenol–formaldehyde resin. At present, the production of wood composites mainly relies on petrochemical-based and formaldehyde-based adhesives such as PF resins and urea–formaldehyde (UF) resins. Phenol–formaldehyde adhesives are used to manufacture plywood, flakeboard, and fiberglass insulation. Phenolic resins occur only in dark, opaque colors and can therefore be used only to manufacture dark-colored products.

Resistance to chemical attack is generally improved by resin impregnation, which protects the underlying wood and reduces movement of liquid into the wood. Resistance to acids can be obtained by impregnating with phenolic resin and to alkalis by impregnating with furfural resin.

The adhesion properties of different natural fillers without the addition of coupling agents by considering the different filler morphology were investigated. The adhesion behavior was determined in a qualitative way from microscopic observation and it was shown that its influence on mechanical properties decreases, since in this type of material tensile strength usually falls.

The reaction of formaldehyde with lignin model compounds in acidic medium is shown to give fast cross-linking of alkali-substituted phenolic and etherified phenolic lignin model compounds at positions meta to the aromatic hydroxyl groups. This reaction differs from the reaction of formaldehyde with phenolic lignin model compounds in alkaline conditions, where the reaction with formaldehyde always occurs at positions ortho/para to the aromatic hydroxyl group.

Lignin degradation products and their sodium salts can be converted into very weak organic acids by treating mineral acids. Most phenols have a  $K_a$  in the neighborhood of  $10^{-10}$  and are thus considerably weaker than the carboxylic acids ( $K_a$  about  $10^{-5}$ ). Most phenols are weaker than carbonic acid ( $\text{CO}_2 + \text{H}_2\text{O}$ ), and, hence, unlike carboxylic acids, do not dissolve in aqueous bicarbonate solutions. Indeed,

phenols are conveniently liberated from their salts by the action of carbonic acid ( $K_a$  about  $10^{-7}$ ).

Organosolv lignin-phenol-formaldehyde (LPF) resins were produced in a two-step preparation with different additions of lignin. The method selected for the manufacture of lignin resins dealt with modification of the lignin by the methylation route. Organosolv lignin-based resins showed comparatively good strength and stiffness. The tensile strength properties of test samples made from organosolv lignin resins were equal to or better than those of test samples made from PF resin only.

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