CHAPTER

8

Thermochemical Processing of Lignocellulosic Biomass

8.1 Introduction

Thermochemical processing uses heat and/or catalysts to convert organic materials into solids, liquids, gases, and/or thermal energy. Four basic thermochemical processes are considered in this chapter: direct combustion, gasification, pyrolysis, and solvolysis. Direct combustion of solid biomass yields hot flue gas that can be used in either the direct-fired or indirect-fired process heaters described in Chapter 6. It can also provide heat to Stirling engines or Rankine steam cycles for the generation of electric power. Gasification yields mostly flammable gases suitable for process heat, power generation, or gaseous and liquid fuel synthesis. Pyrolysis occurs in the absence of oxygen to produce mostly liquid known as bio-oil, which can be used for stationary heat and power applications or upgraded to transportation fuels. It can also be used to depolymerize plant carbohydrates to simple sugars. Solvolysis is the thermal treatment of organic materials in the presence of a solvent. It can be used to extract chemicals, depolymerize and otherwise deconstruct large organic compounds, or even gasify feedstocks.

8.2 Direct Combustion

Combustion is the rapid oxidation of fuel to obtain thermal energy. Because biomass fuels are primarily composed of carbon, hydrogen, and oxygen, the main oxidation products are carbon dioxide and water. Depending on the heating value and moisture content of the fuel, the amount of air used to burn the fuel, and the construction of the furnace, flame temperatures can exceed 1650°C.

Biorenewable Resources: Engineering New Products from Agriculture, Second Edition. Robert C. Brown and Tristan R. Brown.

8.2.1 Fundamentals of Combustion

Solid fuel combustion consists of four steps, illustrated in Figure 8.1: heating and drying, pyrolysis, flaming combustion, and char combustion. Heating and drying of the fuel particle is not normally accompanied by chemical reaction. Water is driven from the fuel particle as the thermal front advances into the interior of the particle. As long as water remains, the temperature of the particle cannot increase enough to initiate pyrolysis, the second step in solid fuel combustion.

Pyrolysis is a complicated series of thermally driven chemical reactions that decompose organic compounds in the fuel. Pyrolysis proceeds at relatively low temperatures, which depend on the type of plant material. Hemicellulose begins to pyrolyze at temperatures between 225°C and 325°C and lignin pyrolysis is initiated between 250°C and 500°C.

The resulting decomposition yields a large variety of volatile organic and inorganic compounds, the types and amounts dependent on the fuel and the heating rate of the fuel. Pyrolysis products include carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and high-molecular-weight compounds that condense to a tarry liquid if cooled before they are able to burn. Fine droplets of these condensable compounds represent much of the smoke associated with smoldering fires. Pyrolysis follows the thermal front through the particle, releasing volatile compounds and leaving behind pores that penetrate to the surface of the particle.

Pyrolysis is very rapid compared to the overall burning process and may be as short as a second for small particles of fuel but can extend to many minutes in wood logs. Although the net result of combustion is oxidation of fuel molecules and the release of heat, neither of these processes occurs to a significant extent during pyrolysis. Indeed, if pyrolysis is to proceed at all, heat must be added to the

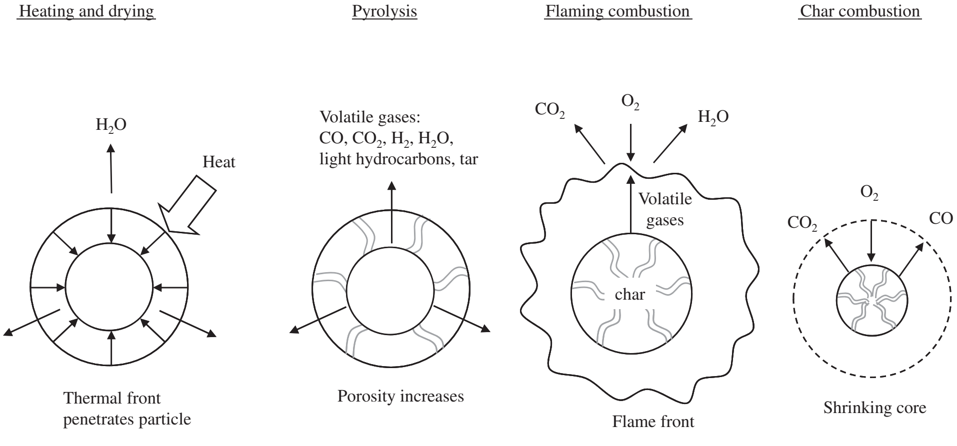


Fig. 8.1 Processes of solid fuel combustion.

fuel. Oxygen is excluded from the pyrolysis zone by the large outflow of gaseous pyrolysis products from the surface of the fuel particle. Only after pyrolysis gases escape the particle and diffuse into the surrounding air are they able to burn. A porous carbonaceous residue known as char remains upon completion of pyrolysis.

Both the volatile gases and the char resulting from pyrolysis can be oxidized if sufficient oxygen is available to them. Oxidation of the volatile gases above the solid fuel results in flaming combustion. The ultimate products of volatile combustion are CO_2 and H_2O although a variety of intermediate chemical compounds can exist in the flame, including CO, condensable organic compounds, and long chains of carbon known as soot. Indeed, hot, glowing soot is responsible for the familiar orange color of wood fires.

Combustion intermediates will be consumed in the flame if sufficient temperature, turbulence, and time are allowed. High combustion temperature assures that chemical reactions will proceed at high rates. Turbulent or vigorous mixing of air with the fuel makes certain that every fuel molecule comes into contact with oxygen molecules. Long residence times for fuel in a combustor allow the fuel to be completely consumed. In the absence of good combustion conditions, a variety of noxious organic compounds can survive the combustion process including CO, soot, polycyclic aromatic hydrocarbons (PAH), and the particularly toxic chlorinated hydrocarbons known as furans and dioxins. In some cases, a poorly operated combustor can produce pollutants from relatively benign fuel molecules.

The next step in combustion of solid fuels is solid–gas reactions of char, also known as glowing combustion, familiar as red-hot embers in a fire. Char is primarily carbon with a small amount of mineral matter interspersed. Char oxidation is controlled by mass transfer of oxygen to the char surface rather than by chemical kinetics, which is very fast at the elevated temperatures of combustion. Depending on the porosity and reactivity of the char and the combustion temperature, oxygen may react with char at the surface of the particle or it may penetrate into the pores before oxidizing char inside the particle. The former situation results in a steadily shrinking core of char, whereas the latter situation produces a constant diameter particle of increasing porosity. Both CO and CO_2 can form at or near the surface of burning char:

$$\mathrm{C} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO} \tag{8.1}$$

$$\mathrm{CO} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO_2} \tag{8.2}$$

These gases escape the immediate vicinity of the char particle where CO is oxidized to CO_2 if sufficient oxygen and temperature are available; otherwise, it appears in the flue gas as a pollutant.

8.2.2 Combustion Equipment

A combustor is a device that converts the chemical energy of fuels into high-temperature exhaust gases. Heat from the high-temperature gases can be employed in a variety of applications, including space heating, drying, and power generation. However, with the exception of kilns used by the cement industry, most solid fuel combustors today are designed to produce either low-pressure steam for process heat or high-pressure steam for power generation. Combustors integrated with steam-raising equipment are called boilers. In some boiler designs, distinct sections exist for combustion, high-temperature heat transfer, and moderate-temperature heat transfer: these are called the furnace, radiative, and convective sections of the boiler, respectively. In other designs, no clear separation between the processes of combustion and heat transfer exists.

Solid fuel combustors, illustrated in Figure 8.2, can generally be categorized as grate-fired systems, suspension burners, or fluidized beds. Grate-fired systems were the first burner systems to be developed, evolving during the late nineteenth and early twentieth centuries into a variety of automated systems. The most common system is the spreader stoker, consisting of a fuel feeder that mechanically or pneumatically flings fuel onto a moving grate where the fuel burns. Much of the ash falls off the end of the moving grate although some fly

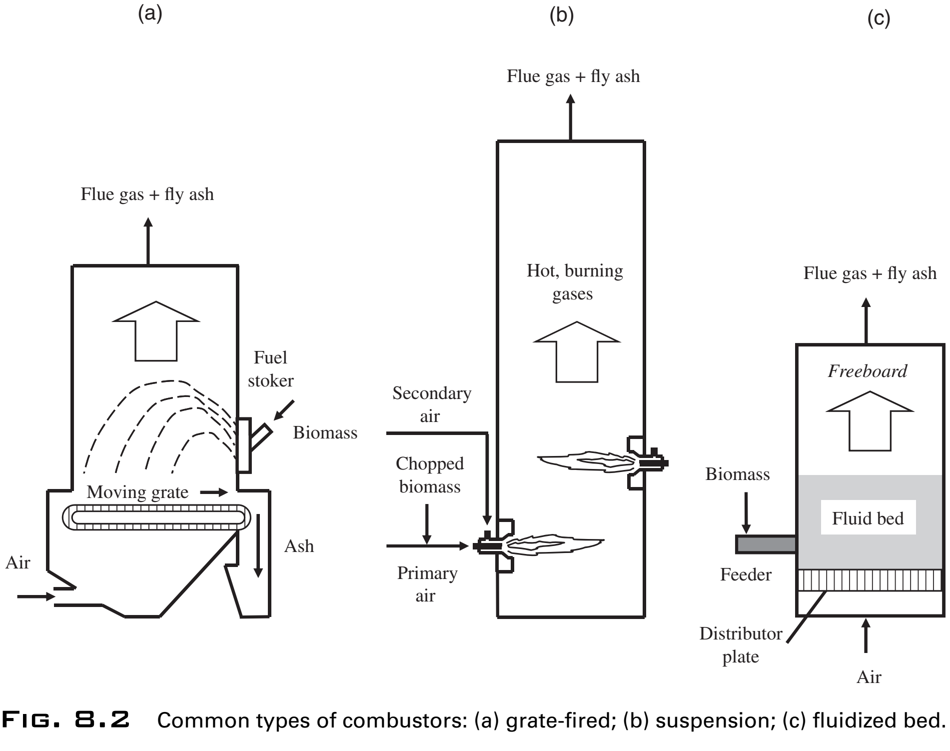


FIG. 8.2 Common types of combustors: (a) grate-fired; (b) suspension; (c) fluidized bed.

ash appears in the flue gas. Grate systems rarely achieve combustion efficiencies exceeding 90%.

Suspension burners were introduced in the 1920s as a means of efficiently burning large quantities of coal pulverized to less than 50 μm particle sizes. Suspension burners suspend the fuel as fine powder in a stream of vertically rising air. The fuel burns in a fireball and radiates heat to tubes that contain water to be converted into steam. Suspension burners, also known as pulverized coal (PC) boilers, have dominated the US power industry since World War II because of their high volumetric heat release rates and their ability to achieve combustion efficiencies, often exceeding 99%. However, they are not well suited to burning coarse particles of biomass fuel and they are notorious generators of nitrogen oxides. Biomass is fed from a bunker through pulverizers designed to reduce fuel particle size enough to burn in suspension. The fuel particles are suspended in the primary airflow and fed to the furnace section of the boiler through burner ports where it burns as a rising fireball. Secondary air injected into the boiler helps complete the combustion process. Heat is absorbed by steam tubes arrayed in banks of heat exchangers (waterwall, superheaters, and economizer) before exiting through a bag house designed to capture ash released from the fuel. Steam produced in the boiler is part of a Rankine power cycle.

Fluidized bed combustors are a recent innovation in boiler design. Air injected into the bottom of the boiler suspends a bed of sand or other granular refractory material producing a turbulent mixture of air and sand. The high rates of heat and mass transfer in this environment are ideal for efficiently burning a variety of fuels. The large thermal mass of the sand bed allows the unit to be operated as low as 850°C, which lowers the emission of nitrogen compounds. A commercial market for fluidized bed boilers was developed during the 1980s, especially for industrial applications.

A whole-tree burner has been proposed for electrical utility steam raising. The advantage of this approach is minimization of field processing and handling and the elimination of fuel chipping, which can save about 35% of the cost of harvesting and handling woody fuels.

A variety of biomass materials have proven suitable for direct combustion, including whole trees, wood chips, forestry residue, agricultural residue, pulp and paper refuse, food processing wastes, municipal solid waste, and straws and grasses. Wood and wood wastes dominate the biomass-to-power market in the United States and much of the rest of the world. Power plants in California have direct-fired agricultural wastes, and Denmark has a number of commercial plants that burn straw.

Direct combustion has the advantage that it employs commercially well-developed technology. There are a number of vendors who supply turnkey systems and considerable operating experience exists both in the United States and abroad. However, there are three prominent disadvantages with direct firing. These include penalties associated with burning high-moisture fuels, agglomeration and ash fouling due to alkali compounds in biomass, and relatively low thermodynamic efficiencies for steam power plants of the size appropriate to biomass power.

The moisture in biomass degrades boiler performance for two reasons. First, the energy required to vaporize fuel moisture can only be recovered if exhaust gases are cooled sufficiently to condense the water vapor in this gas. Although this procedure would result in very high thermal efficiencies for a boiler burning even very high-moisture fuels, it is not commonly done in practice because the condensate is often corrosive to boiler tubes. Accordingly, most direct-combustion systems are penalized by moisture in the fuel. Second, high-moisture fuels simply do not burn well because the process of fuel drying suppresses fuel temperatures below that required for ignition. Water contents exceeding 30% are unacceptable in most boilers for this reason. Fluidized bed combustors, however, because of the enormous thermal mass associated with the hot bed material, can accept biomass with moisture content as high as 50% although even fluidized beds are penalized in thermal efficiency by the presence of this moisture. Depending on moisture content, as much as 15% of the heating value of biomass is required to dry the fuel. Obviously, field drying of biomass is desired to reduce both transportation costs and heating penalties within the boiler.

Alkali in biomass fuels presents a difficult problem for direct combustion systems. Compounds of alkali metals, such as potassium and sodium salts, are common in rapidly growing plant tissues. Annual biomass crops contain large quantities of alkali, while the old-growth parts of perennial biomass contain relatively small quantities of alkali. These alkali compounds appear as oxides in the residue left after combustion of volatiles and char. Alkali vapors may combine with sulfur and silica to form low-melting-point compounds. These sticky compounds bind ash particles to fuel grates and heat exchanger surfaces. Boiler performance degrades as airflow and heat transfer are restricted by ash deposits. Boilers that fire straw, which contain both high silica and alkali, have experienced serious problems in slagging and fouling as well as high-temperature corrosion unless steam temperatures are kept relatively low (less than 500°C).

As an alternative to completely replacing coal with biomass fuel in a boiler, mixtures of biomass and coal can be burned together in a process known as cofiring. Cofiring offers several advantages for industrial boilers. Industries that generate large quantities of biomass wastes, such as lumber mills or pulp and paper companies, can use cofiring as an alternative to costly landfilling of wastes. Federal regulations also make cofiring attractive. The New Source Performance Standards, which limits particulate emissions from large coal-fired industrial boilers to 0.05 lb/MMBtu, doubles this allowance in cofired boilers in which the capacity factor for biomass exceeds 10%. Adopting cofiring is a good option for companies that are slightly out of compliance with their coal-fired boilers. Similarly, a relatively inexpensive method for a company to reduce sulfur emissions from its boilers is to cofire with biomass, which contains much less sulfur than coal. Cofiring capability also provides fuel flexibility and reduces ash fouling problems associated with using only biomass as fuel.

The principal disadvantages of cofiring relate to the characteristics of biomass fuels. Because of the lower energy density and higher moisture content of biomass, the steam-generating capacity of cofired boilers is often reduced. Also, the elemental composition of fly ash from biomass is distinct from that of coal fly ash. Utilities are concerned that comingled biomass and coal ash will not meet the American Society for Testing and Materials (ASTM) definition of fly ash that is acceptable for concrete admixtures, thus eliminating an important market for this combustion byproduct.

It is generally recommended that total fuel (single or mix) alkali content be limited to less than 0.17–0.34 kg/GJ (0.4–0.8 lb/MMBtu), which translates to only 5–15% cofiring of biomass with coal. Also, furnace temperatures should be kept below 980°C to help prevent the buildup of alkali-containing mineral combinations known as eutectics. At higher temperatures, molten eutectics bind dirt and other particulates to form slag and fouling deposits.

The best wood-fired power plants, which are typically 20–100 MW in capacity, have heat rates exceeding 12 500 Btu/kWh. In contrast, large, coal-fired power plants have heat rates of only 10 250 Btu/kWh. The relatively low thermodynamic efficiency of steam power plants at the sizes of relevance to biomass power systems may ultimately limit the use of direct combustion to convert biomass fuels to useful energy.

8.3 Gasification

Gasification is the conversion of solid, carbon-rich materials under oxygen-starved conditions and elevated temperatures (typically 750–1500°C) into flammable gas mixtures consisting of carbon monoxide (CO), hydrogen (H_2), methane (CH_4), nitrogen (N_2), carbon dioxide (CO_2), and smaller quantities of higher hydrocarbons and inorganic contaminants like hydrogen sulfide (H_2S) and ammonia (NH_3). The gas mixture is sometimes called syngas (short for synthesis gas), but the raw gas is more properly referred to as producer gas until it has been cleaned and conditioned for use in chemical synthesis.

The release of volatiles from solid fuel is endothermic and requires either the simultaneous burning of part of the fuel or the delivery of an external source of heat to drive the process. Gasification should not be confused with anaerobic digestion, the microbial degradation of biomass to a flammable gas mixture of mostly CH_4 and N_2, a process described in Chapter 9.

Gasification was placed into commercial practice as early as 1812 when coal was converted to gas for illumination (known as manufactured gas or town gas) in

England. This technology was widely adopted in industrialized nations and was employed in the United States as late as the 1950s when interstate pipelines made inexpensive supplies of natural gas available. Some places, such as China and South Africa, still manufacture gas from coal.

The high volatile content of biomass (70–90 wt%) compared to coal (typically 30–40 wt%) and the high reactivity of its char make biomass an ideal gasification feedstock. However, issues of cost and convenience of biomass gasification have limited its applications to special situations and niche markets. For example, in response to petroleum shortages during World War II, over one million small-scale wood gasifiers were built to supply low-enthalpy gas for automobiles and steam boilers. These were abandoned soon after the war.

Not only can producer gas be used for generation of heat and power but also can serve as feedstock for production of liquid fuels and chemicals. Because of this flexibility of application, gasification has been proposed as the basis for "energy refineries" that would provide a variety of energy and chemical products, including electricity and transportation fuels.

8.3.1 Fundamentals of Gasification

Figure 8.3 illustrates the several steps of gasification: heating and drying, pyrolysis, solid–gas reactions that consume char, and gas-phase reactions that adjust the final chemical composition of the producer gas. Drying and pyrolysis are similar to the corresponding processes for direct combustion described in the previous section. Pyrolysis begins between 300°C and 400°C and produces the intermediate products of char: gases (mainly CO, CO_2, H_2, and light hydrocarbons) and condensable vapor (including water, methanol, acetic acid, acetone, and heavy hydrocarbons). The distribution of these products depends on chemical composition of the fuel, the heating rate, and the temperature achieved in the reactor. However, the total pyrolysis yield of pyrolysis products and the amount of char residue can be roughly

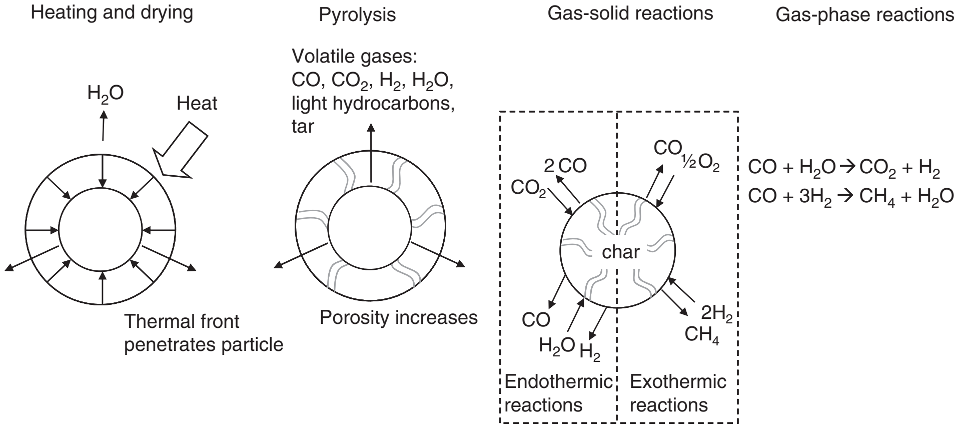


FIG. 8.3 Processes of thermal gasification.

estimated from the proximate analysis of the fuel. The fuel's volatile matter roughly corresponds to the pyrolysis yield while the combination of fixed carbon and ash content can be used to estimate the char yield.

Heating and drying are endothermic processes, requiring a source of heat to drive them. This heat can be supplied by an external source in a process called indirectly heated gasification. More typically, a small amount of air or oxygen (typically not more than 25% of the stoichiometric requirement for complete combustion of the fuel) is admitted for the purpose of partial oxidation, which releases sufficient heat for drying and pyrolysis as well as for the subsequent endothermic chemical reactions described below.

The third step of gasification is gas–solid reactions. These reactions convert solid carbon into gaseous CO, H_2, and CH_4:

$$\text{Carbon–oxygen reaction: } C + \frac{1}{2}O_2 \leftrightarrow CO \quad \Delta H_R = -110.5 \text{ MJ/kmol} \tag{8.3}$$

$$\text{Boudouard reaction: } C + CO_2 \leftrightarrow 2CO \quad \Delta H_R = 172.4 \text{ MJ/kmol} \tag{8.4}$$

$$\text{Carbon–water reaction: } C + H_2O \leftrightarrow H_2 + CO \quad \Delta H_R = 131.3 \text{ MJ/kmol} \tag{8.5}$$

$$\text{Hydrogenation reaction: } C + 2H_2 \leftrightarrow CH_4 \quad \Delta H_R = -74.8 \text{ MJ/kmol} \tag{8.6}$$

The first of these, known as the carbon–oxygen reaction, is strongly exothermic and is important in supplying the energy requirements for drying, pyrolysis, and endothermic solid–gas reactions. The hydrogenation reaction also contributes to the energy requirements of the gasifier, although significantly more char reacts with oxygen than hydrogen in the typical air-blown gasifier.

The fourth step of gasification is gas-phase reactions, which determine the final mix of gaseous products:

$$\text{Water–as shift reaction: } CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta H_R = -41.1 \text{ MJ/kmol} \tag{8.7}$$

$$\text{Methanation: } CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H_R = -206.1 \text{ MJ/kmol} \tag{8.8}$$

The final gas composition is strongly dependent on the amount of oxygen and steam admitted to the reactor as well as the time and temperature of reaction. For sufficiently long reaction times, chemical equilibrium is attained and the products are essentially limited to the light gases CO, CO_2, H_2, and CH_4 (and nitrogen if air was used as a source of oxygen). Analysis of the chemical thermodynamics of these six gasification reactions reveals that low temperatures and high pressures favor the formation of CH_4, whereas high temperatures and low pressures favor the formation of H2 and CO.

Often gasifier temperatures and reaction times are not sufficient to attain chemical equilibrium, and the producer gas contains various amounts of light hydrocarbons such as C_2H_2 and C_2H_4 as well as up to 10 wt% heavy hydrocarbons that condense to form a black, viscous liquid known as "tar." This latter product is undesirable as it can block valves and filters and interferes with downstream conversion processes. Steam injection and addition of catalysts to the reactor are sometimes used to shift products toward lower-molecular-weight compounds.

8.3.2 Gasification Systems

Gasifiers are generally classified according to the method of contacting fuel and gas. The four main types of interest to biomass gasification are updraft (countercurrent), downdraft (concurrent), fluidized bed, and entrained flow. These are illustrated in Figure 8.4, and their performance characteristics are summarized in Table 8.1.

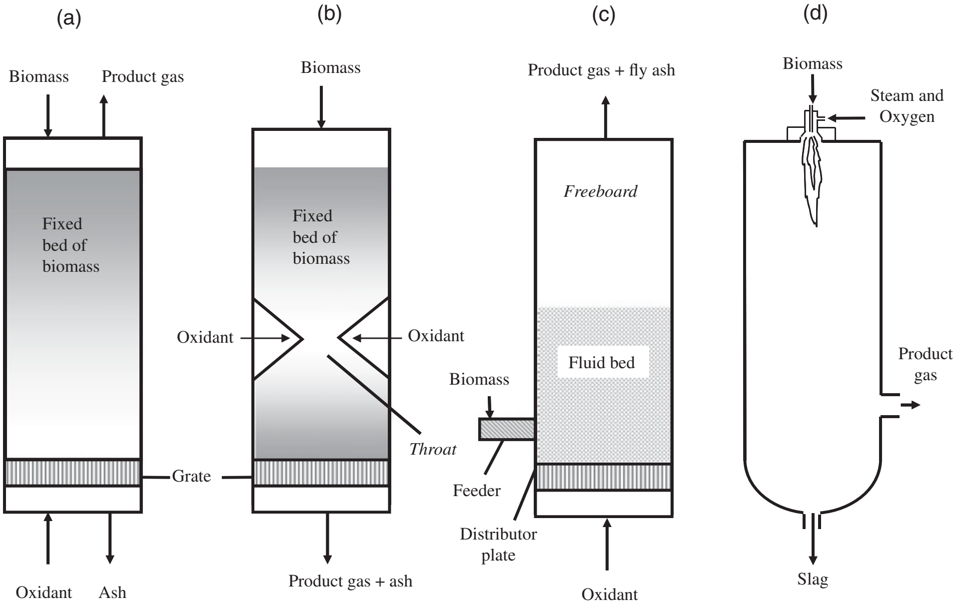


FIG. 8.4 Common types of biomass gasifiers: (a) updraft; (b) downdraft; (c) fluidized bed; (d) entrained flow.

Table 8.1 Producer gas composition from various kinds of gasifiers

	Gaseous Constituents (vol% dry)						Gas Quality	
Gasifier Type	H_2	CO	CO_2	CH_4	N_2	HHV (MJ/m^3)	Tars	Dust
Air-blown updraft	11	24	9	3	53	5.5	High (~50 g/m^3)	Low
Air-blown downdraft	17	21	13	1	48	5.7	Low (~1 g/m^3)	Medium
Air-blown fluidized bed	9	14	20	7	50	5.4	Medium (~10 g/m^3)	High
Oxygen-blown downdraft	32	48	15	2	3	10.4	Low (~1 g/m^3)	Low
Indirectly heated fluidized bed	31	48	0	21	0	17.4	Medium (~10 g/m^3)	High

Source: Bridgwater, A.V. (1995) The technical and economic feasibility of biomass gasification for power generation. *Fuel*, 74, 631—653; Milne, T.A., Abatzoglou, N., and Evans, R.J. (1998) Biomass gasifier "Tars": their nature, formation, and conversion. National Renewable Energy Laboratory Report, NREL/TP-570-25357.

Updraft gasifiers, illustrated in Figure 8.4a, are the simplest as well as the first type of gasifier developed. They were a natural evolution from charcoal kilns, which yield smoky yet flammable gas as a waste product, and blast furnaces, which generate product gas that reduces ore to metallic iron. Updraft gasifiers are little more than grate furnaces with chipped fuel admitted from above and insufficient air for complete combustion entering from below. Above the grate, where air first contacts the fuel, combustion occurs and very high temperatures are produced. Although the gas flow is depleted of oxygen higher in the fuel bed, hot H_2O and CO_2 from combustion near the grate reduce char to H_2 and CO. These reactions cool the gas, but temperatures are still high enough to heat, dry, and pyrolyze the fuel moving down toward the grate. Of course, pyrolysis releases both condensable and noncondensable gases, and the producer gas leaving an updraft gasifier contains large quantities of tars, on the order of 50 g/m^3. As a result, updraft gasifiers are generally not strong candidates for biomass energy applications.

In downdraft gasifiers, fuel and gas move in the same direction. Downdraft gasifiers appear to have been developed near the end of the nineteenth century after the introduction of induced draft fans, which allowed air to be drawn downward through a gasifier in the same direction as the gravity-fed fuel. As shown in Figure 8.4b, contemporary designs usually add an arrangement of tuyeres that admit air or oxygen directly into a region known as the throat where combustion forms a bed of hot char. This design assures that condensable gases released during pyrolysis are forced to flow through the hot char bed, where tars are cracked. The producer gas is relatively free of tar (less than 1 g/m^3), making it a satisfactory fuel for engines. A disadvantage is the need for tightly controlled fuel properties (particles sized to between 1 and 30 cm, low ash content, and moisture less than

30%). Another disadvantage is a tendency for slagging or sintering of ash in the concentrated oxidation zone. Rotating ash grates or similar mechanisms can solve this problem. Furthermore, incorporation of a throat region limits the maximum size of downdraft gasifiers to about 400 kg/h.

In a fluidized bed gasifier, illustrated in Figure 8.4c, a gas stream passes vertically upward through a bed of inert particulate material to form a turbulent mixture of gas and solid. Fuel is added at such a rate that it is only a few percent by weight of the bed inventory. Unlike the updraft and downdraft gasifiers, no segregated regions of combustion, pyrolysis, and tar cracking exist. The violent stirring action makes the bed uniform in temperature and composition, with the result that gasification occurs simultaneously at all locations in the bed. Typically a fluidized gasifier operates in the range of 700–850°C. By injecting fuel in the base of the bed, much of the tar can be cracked within the fluidized bed. However, a large insulated space above the bed, known as the freeboard, is usually included to promote additional tar cracking as well as more complete conversion of char. Nevertheless, tar production is intermediate between updraft and downdraft gasifiers (about 10 g/m^3). Fluidized beds are attractive for biomass gasification. They are able to process a wide variety of fuels including those of high moisture and small size. They are easily scaled to large sizes suitable for electric power production. Disadvantages include relatively high power consumption to move gas through the fluidized bed; high exit gas temperatures, which complicate efficient energy recovery; and relatively high particulate burdens in the gas due to the abrasive forces acting within the fluidized bed.

An entrained flow gasifier, illustrated in Figure 8.4d, injects powdered fuel into a gas flow. Entrained flow reactors are ideal for steam–oxygen gasification of coal at temperatures of 1200–1500°C. If the fuel is finely powdered, these high temperatures assure excellent carbon conversion (approaching 100%) and low tar production even for the short residence times (a few seconds) characteristic of entrained flow gasifiers. The technology is attractive for solid fuels like coal or coke that are easily pulverized, but their use is problematic for biomass, which tends to shred into fibers rather than break into fine powders. Furthermore, the low energy density and high sintering potential of biomass make it difficult to achieve the high temperatures characteristic of entrained flow gasifiers. The high carbon conversion efficiency of entrained flow gasifiers has encouraged researchers to explore ways to utilize biomass feedstocks with them.

One approach, known as torrefaction, slowly heats the biomass in the absence of oxygen at temperatures in the range of 200–350°C. Torrefaction is accompanied by small losses in mass and energy compared to the raw biomass. Torrefied biomass is both more brittle and less hydroscopic than raw biomass, allowing it to be pulverized and mixed with water to produce a slurry suitable for injection into an entrained flow gasifier.

Another approach, known as fast pyrolysis, rapidly heats biomass to temperatures between 350°C and 550°C for the purpose of converting as much as 70 wt% of the biomass into a liquid known as bio-oil and charcoal known as biochar. The bio-oil or a slurry of bio-oil and biochar can be injected under high pressure into an entrained flow gasifier to form a fine spray of liquid droplets that are rapidly gasified.

The fuel:air ratio is the single most important parameter for determining gasifier performance. The conversion efficiency and gas quality of downdraft gasifiers can be superior to fluidized bed gasifiers because they utilize higher fuel/air ratios. Fluidized bed gasifiers, on the other hand, can generally handle a wider range of biomass feedstocks with higher moisture content.

Recent research in biomass gasification has focused on improving the heating value of product gas. Conventional gasification admits sufficient air or oxygen to the reactor to burn part of the fuel thus releasing heat to support pyrolysis of the rest of the fuel. Gas produced in air-blown biomass gasifiers typically has heating value that is only 10–20% that of natural gas. This low heating value is largely the result of nitrogen diluting the fuel gas. Oxygen can be used as the fluidization agent, but high capital costs preclude this from consideration for small-scale energy systems.

Indirectly heated gasification can improve gas heating value by physically separating combustion and pyrolysis. As a result, the products of combustion do not appear in the fuel gas. Higher heating values of 14 200 $\mathrm{kJ/m^3}$ or higher are expected. Several schemes have been suggested for transporting heat from the combustion reactor to the pyrolysis reactor. These include transferring hot solids from the combustor to the pyrolyzer, transferring a chemically regenerative heat carrier between two reactors, transferring heat through a wall common to the reactors, and storing heat in high-temperature phase-change material.

The thermodynamic efficiency of gasifiers is strongly dependent on the kind of gasifier and how the product gas is employed. Some high-temperature, high-pressure gasifiers are able to convert 90% of the chemical energy of solid fuels into chemical and sensible heat of the product gas. However, these high efficiencies come at high capital and operating costs. Most biomass gasifiers have conversion efficiencies ranging between 70% and 80%. In some applications, such as process heaters or driers, both the chemical and sensible heat of the product gas can be utilized. In many power applications, though, the hot product gas must be cooled before it is utilized; thus, the sensible heat of the gas is lost. In this case, "cold gas" efficiency can be as low as 50–60%. Whether the heat removed from the product gas can be recovered for other applications, like steam raising or fuel drying, ultimately determines which of these conversion efficiencies is most meaningful. Gas cleaning to remove tar and particulate matter also has a small negative impact on gasifier efficiency since it removes flammable constituents from the gas (tar and char particles) and generally requires a small amount of energy to run pumps.

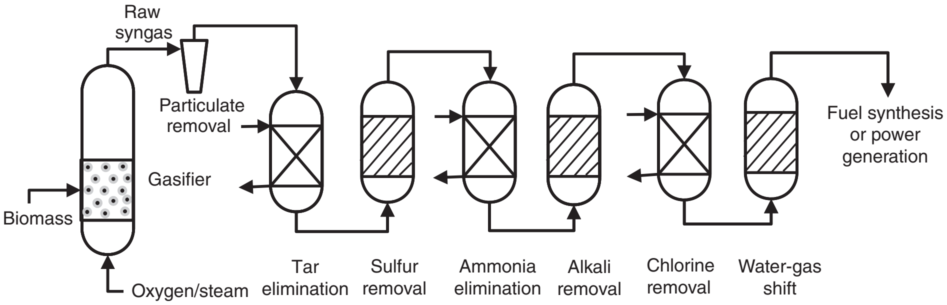


FIG. 8.5 Gas cleaning and conditioning before fuel synthesis or power generation may include several stages, including tar elimination, sulfur removal, ammonia elimination, alkali and chlorine removal, and water–gas shift reaction.

8.3.3 Gas Conditioning

Flammable gas mixtures, whether derived from producer gas, anaerobic digesters, or natural gas, are generally not directly usable as fuel gas or chemical feedstock without some degree of gas conditioning. Gas conditioning includes gas cleaning to remove contaminants and gas enrichment of certain chemical constituents, especially hydrogen (see Figure 8.5). Gas streams from biomass gasification almost always require some level of gas cleaning to meet limits on contaminants in power and fuel synthesis applications. Contaminants to be managed include particulate matter, tar, sulfur, nitrogen, alkali metals, and chlorine (contaminant limits for fuel cell applications are found in Table 6.1, while Table 8.2 contains limits for other applications). Often each type of contaminant requires a separate unit operation to remove or eliminate it from the gas stream although sometimes a single operation is effective against multiple contaminants.

Particulate matter is divided solids, usually in the size range of 0.1–100 μm, suspended in the gas stream. In the case of producer gas, it is primarily mineral

Table 8.2 Gas cleaning levels for producer gas required for select power and fuel synthesis applications

	Application			
Contaminant	IC Engine	Gas Turbine	Methanol Synthesis	FT Synthesis
Particulate	<50 mg/m^3	<30 mg/m^3	<0.02 mg/m^3	Not detectable
Tars	<100 mg/m^3	<8 mg/m^3	<0.1 mg/m^3	<10 ppb
Sulfur	–	<20 ppm	<1 mg/m^3	<10 ppb
Nitrogen	–	<50 ppm	<0.1 mg/m^3	<20 ppb
Alkali	–	<24 ppb	–	<10 ppb
Chloride	–	<1 ppm	<0.1 mg/m^3	<10 ppb

Source: Woolcock, P. and Brown, R.C. (2013) A review of cleaning technologies for biomass-derived syngas. *Biomass and Bioenergy*, 52, 54–84.

matter (ash) and unburned elemental carbon (char) released from gasifying biomass although it may also include inorganic compounds originating from minerals like sand or limestone, which are sometimes added to gasifiers to control their operation. It should be noted that coarser particulate matter may fall to the bottom of a gasifier, in which case it is called bottom ash (although it also contains char) and in very high temperature gasifiers, much of the particulate matter melts and leaves the bottom of the gasifier as molten slag.

Particulate matter is usually the first contaminant to be removed from producer gas because it can interfere with subsequent unit operations. Problems include clogging pipes and orifices and coating heat transfer and chemical catalyst surfaces (ash fouling). The particulate matter also can transport sulfur and nitrogen species that poison catalysts. Particulate matter is removed immediately downstream of the gasifier by gas cyclones operated at temperatures high enough to avoid condensation of tarry compounds in the gas. Cyclones can be very effective down to particulate sizes of about 10 μm, but finer particles are not substantially removed. Because of the high temperatures involved, additional filtration of the finest particles requires ceramic or metal alloy barrier filters or moving bed granular filters.

Tar is any organic compound that condenses from producer gas when it is cooled to room temperature. In appearance, it is a dark, viscous liquid. Tar consists of organic compounds ranging from light oxygenated compounds to PAH. A well-designed gasifier has a high-temperature zone through which pyrolysis products pass, allowing tars to thermally decompose ("crack") into the low-molecular gases predicted by equilibrium theory. Although increasing residence times and temperatures reduce tar yields, those compounds that remain are refractory to further decomposition. Almost all gasifiers produce some level of tar in the product gas stream.

Tar cannot be tolerated in many downstream applications, including internal combustion engines, fuel cells, and chemical synthesis reactors. Tar can deposit on surfaces in filters, heat exchangers, and engines where they reduce component performance and increase maintenance requirements.

Tar can be eliminated from producer gas by either of two methods. One method reacts the gas stream with steam at high temperature to convert the tar to CO and H_2. This "cracking" of tar can be accomplished by raising the gas temperatures above 1000°C. Such high temperatures are not easily achieved in most biomass gasifiers. The use of catalysts, either in the gasifier or immediately after removal of particulate matter, allows tar cracking to occur at much lower temperatures, in the range of 600–800°C. Although catalytic cracking is effective in reducing tar to low levels, the catalysts are susceptible to fouling by the deposition of coke, a tar cracking byproduct, and poisoning by inorganic contaminants in the gas stream.

A simpler approach to gas cleaning scrubs the gas stream with water or oil, which is effective in removing both tar and particulate matter from the gas. The scrubbing liquid is either sprayed countercurrently into the gas stream as a fine mist or flowed downward by gravity over packing materials in a gas scrubbing column through which the gas flows upward. In either case, the scrubbing liquid both cools the gas, causing the tar to condense as aerosol droplets, and intercepts both solid particles of char and liquid droplets of tar, removing them from the gas flow. The tar and particulate-laden scrubbing liquid exits the scrubbing column for cooling and separation of the contaminants in a settling tank before being reinjected into the dirty gas stream. Because tar contributes to the chemical enthalpy of the producer gas, its removal reduces the overall efficiency of the gasification process (as compared to tar cracking, which recovers the chemical enthalpy of the tar). In fact, the tar recovered by scrubbing becomes a waste disposal problem unless it can be recycled to the gasifier and cracked there. Scrubbing the gas stream with water also produces water contaminated with tar, which requires an additional unit operation of wastewater treatment.

Sulfur appears in producer gas mostly as hydrogen sulfide (H_2S) with lesser amounts of carbonyl sulfide (COS). Although biomass contains significantly less sulfur than coal, it is often high enough to poison many catalysts used to upgrade producer gas to fuel. In some instances sulfur may be limited to a few parts per billion levels (see Table 8.2).

Several gas cleaning technologies have been developed to remove sulfur and other acid gases such as hydrogen chloride. These include both dry- and liquid-based processes operating at a temperature range from subzero to several hundred degrees Celsius. Attempts to remove contaminants at high temperatures (hot gas cleaning) focus on the use of dry sorbents. The challenge is reducing sulfur concentration in the gas stream to as little as a 10 parts per billion.

Most nitrogen from biomass gasification is derived from the thermal decomposition of protein. If chemical equilibrium was achieved during gasification, virtually all of this nitrogen would appear as harmless molecular nitrogen (N_2). Instead, nitrogen in biomass is partitioned between N_2, ammonia (NH_3), and a small amount of hydrogen cyanide. These nitrogen compounds can be reacted with steam over a catalyst to reduce them to molecular nitrogen in a manner similar to the steam reforming of tar to light gases. In fact, tar and nitrogen compounds are sometimes decomposed in the same catalytic reactor. Relatively inexpensive Ni-based reforming catalysts can reduce ammonia in producer gas by over 75%. However, sulfur in the gas stream can quickly deactivate Ni-based catalysts unless they are protected by a guard bed of sulfur sorbent. Alternatively, since ammonia is soluble in slightly acidic solutions, it can be scrubbed from producer gas by a pH-adjusted water spray in a manner similar to the scrubbing of tar from producer gas.

Alkali metals commonly found in biomass include potassium and sodium. Potassium, an important nutrient in crop growth, is particularly prominent in biomass especially herbaceous feedstocks like grasses and corn stover. When biomass is heated, alkali metal compounds melt and some fraction of those evaporate at temperatures as low as 600°C. Alkali compounds transported out of the reactor, usually in the form of chlorides, hydroxides, and sulfates, can condense on surfaces cooler than the gas stream, such as heat transfer surfaces, and form a sticky liquid film that adheres to fly ash. Over time, this leads to serious ash fouling. Furthermore, alkali can poison catalysts and corrode gas turbine blades even at very low concentrations.

Alkali can be removed from gas streams by cooling below its condensation temperature and then scrubbing out the resulting particulate matter in a manner similar to removal of tar aerosols. This can be done in conjunction with other unit operations of gas cleaning. Alternatively, removal of alkali from hot gas streams can be accomplished with solid sorbents known as getters. This approach is particularly attractive for gas turbines and certain fuel cell applications where cooling of the producer gas is to be avoided for thermodynamic reasons.

The occurrence of chlorine in biomass is species dependent. During combustion, most chloride is released as hydrochloric acid (HCl) although some reacts with alkali metals to form volatile salts. Both acid and salts readily absorb in water to form corrosive solutions that rapidly corrode metal surfaces in processing equipment. This high solubility is the key to its removal using water scrubbers, which may simultaneously remove other contaminants. A number of sodium-rich minerals have been employed as HCl sorbent in hot gas cleaning operations.

Even after gas cleaning, the producer gas may require additional processing to obtain gas composition consistent with power generation or chemical synthesis. For example, most fuel cells are dependent on hydrogen-rich gas streams for their operation. Pure hydrogen fuel has even been envisioned for gas turbine cycles in an effort to reduce greenhouse gas emissions into the atmosphere. Also, producer gas to be used for catalytic synthesis of hydrocarbons typically requires H_2:CO ratios to be increased to 2:1, after which it truly can be called "syngas."

Hydrogen enrichment can be achieved by combining steam with producer gas and passing the gas mixture over a catalytic bed. This promotes the reduction of water to hydrogen and the oxidation of carbon monoxide to carbon dioxide, a process known as the water–gas shift reaction (see Equation 8.7).

The water–gas shift reaction is exothermic, which means it is favored at low temperatures. To achieve commercially significant reaction rates, the process is conducted in two stages: a high-temperature reactor to rapidly move the reaction forward and a low-temperature reaction to achieve a higher overall yield of hydrogen. The water–gas shift reaction is widely employed by ammonia manufacturers, petroleum refiners, and other industries to produce hydrogen from natural gas and other fossil fuels.

8.3.4 Chemical Synthesis from Syngas

Clean, conditioned syngas, consisting of approximately two moles of hydrogen for every mole of carbon monoxide, provides the carbon, hydrogen, and energy necessary to synthesize hydrocarbons as well as the oxygen necessary to synthesize oxygenated organic compounds like methanol and ethanol. Organic synthesis from this simple gaseous mixture was originally developed for the conversion of coal into methanol or synthetic gasoline. The process can also employ biorenewable resources as feedstock although the current low cost of fossil fuels has hampered the manufacture of biobased products by this method.

Two distinct approaches to convert syngas to chemicals are possible. The traditional approach involves the moderate temperature, high-pressure catalytic synthesis of methanol or synthetic gasoline. A more recently developed approach employs microorganisms that are able to grow on one-carbon compounds to convert syngas into organic acids or alcohols.

Catalytic Synthesis

Catalysts have been developed for the synthesis of a wide variety of chemicals from syngas. Those considered in this section include methanol, ammonia, dimethyl ether (DME), mixed alcohols, and Fischer–Tropsch (F–T) liquids.

Methanol (CH_3OH) is commercially produced by reacting syngas over a copper–zinc catalyst at 5–10 MPa and 250°C.

$$CO + 2H_2 \rightarrow CH_3OH \tag{8.9}$$

From the standpoint of cost, methanol is among the most attractive fuel production options for syngas. It is unlikely to find wide acceptance as fuel, though, because of its toxicity. It remains one of the largest commodity chemicals produced in the world. It is the building block for a wide variety of chemicals including synthetic gasoline via DME, as subsequently described.

Ammonia (NH_3) has been proposed as a propane-like fuel that can be produced from hydrogen and distributed as a compressed liquid using production and distribution technology developed for the nitrogen fertilizer industry. The exothermic reaction of hydrogen and nitrogen to produce ammonia favors high pressures and low temperatures:

$$N2 + 3H_2 \rightarrow 2NH_3 \tag{8.10}$$

Complete reaction would require pressures of 80 MPa and reaction temperatures below 200°C. Practical considerations require operation at higher temperatures and lower pressures. The Haber–Bosch process employs an iron-based catalyst at 20 MPa and 500°C to achieve a relatively modest 10–20% molar yield of ammonia, but the process is made economically feasible through recycling of unreacted gases and energy recovery. Sulfur readily poisons the iron-based catalyst used to facilitate this reaction. Because the hydrogen is generally obtained through steam reforming and water–gas shift reactions that also employ sulfur-sensitive catalysts, sulfur removal is usually accomplished ahead of hydrogen production.

The energy lost in transforming three molecules of hydrogen into two molecules ammonia would appear to be relatively modest: 87% of the chemical energy of the hydrogen appears in the chemical energy of the ammonia. However, the nitrogen for this fuel comes from liquefying air, an energy intensive process. Several energy intensive processes in ammonia manufacture bring the energy tab to 650 kJ/mol of ammonia produced. This may be justified when the product is fertilizer, but it does not compare favorably to the 316 kJ/mol of energy released when the ammonia is burned as fuel.

Methane can be catalytically generated from syngas by reacting it over nickel catalyst at low temperature and high pressure to promote the exothermic reactions:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{8.11}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{8.12}$$

Synthetic natural gas from coal by this process has been demonstrated on the commercial scale although the price of production is too high to be more widely deployed at this time.

Post-gasification synthesis to methane could be eliminated if methane was generated as the main product of gasification. This can be achieved by gasifying biomass in the presence of externally generated hydrogen, which reacts with carbon and carbon monoxide to form methane:

$$C + 2H_2 \rightarrow CH_4 \tag{8.13}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{8.14}$$

Known as hydrogasification, this exothermic process requires catalysts and operation at low temperatures and high pressures. The process has not achieved commercial status because suitable low-cost catalysts have yet to be developed.

Dimethyl ether has the chemical formula CH_3OCH_3. It can be produced either directly from syngas or indirectly through the dehydration of syngas-derived methanol by reactions at high pressure over catalysts. DME can be dehydrated over a zeolite catalyst to yield gasoline by the energy efficient “methanol-to-gasoline” (MTG) process developed by Mobil. MTG has been commercially demonstrated in New Zealand using syngas generated from the steam reforming of natural gas. Although yielding high-octane gasoline, the products include a high-melting-point hydrocarbon that can clog fuel injectors.

Synthesis of ethanol (C_2H_5OH) and higher alcohols is also possible from syngas. Efforts in Germany during World War II to develop alternative motor fuels discovered that iron-based catalysts could yield appreciable quantities of water-soluble alcohols from syngas. Some researchers have advocated the use of “mixed alcohols” as transportation fuels because the product typically contains a mixture of methanol, ethanol, 1-propanol, and 2-propanol. The process was commercialized in Germany between 1935 and 1945 but eventually abandoned because of the increased availability of inexpensive petroleum. Working at pressures of around 5 MPa and temperatures in the range of 220–370°C, researchers have developed catalysts with selectivity to alcohols of over 95%, but production of pure ethanol has been elusive.

Mixed alcohol synthesis has not been commercialized due to poor product selectivity and low syngas conversion. On a single pass, about 10% of syngas gets converted with most of the product composed of methanol. Recycling methanol aids the production of higher alcohols. Generating revenue from higher alcohols would be important for the successful commercialization of this process.

Fischer–Tropsch liquids are synthetic alkane hydrocarbons produced from syngas by the action of metal catalysts at elevated pressures. Depending on the types and quantities of F–T products desired, either low- (200–240°C) or high-temperature (300–350°C) synthesis is used with either an iron (Fe) or cobalt catalyst (Co). Additional processing of the F–T products yields diesel or gasoline. F–T technology was extensively developed and commercialized in Germany during World War II when it was denied access to petroleum-rich regions of the world. Likewise, when South Africa faced a world oil embargo during its era of apartheid, it employed F–T technology to sustain its national economy from indigenous sources of coal. F–T catalysts are readily poisoned by sulfur, nitrogen, and chlorine at concentrations below one part per million. Thus, removal of contaminants ahead of the synthesis reactors is an important and expensive part of F–T synfuels' plant.

Biocatalytic Synthesis

Certain microorganisms, known as unicarbontrophs, are able to grow on one-carbon compounds as the sole source of carbon and energy. These include some of the same microorganisms involved in anaerobic digestion of polysaccharides. Acetogens can convert CO or mixtures of CO and H_2 to fatty acids and, in some cases, alcohols. Both types of microorganisms are thought to involve a common reaction pathway that disproportionates CO and produces acetyl CoA as an intermediate. Methanogens can produce methane from mixtures of CO, CO_2, and H_2. Thus, syngas can be biologically converted to a variety of fuels and chemicals including ethanol, methane, acetic acid, butyric acid, and butanol.

Clostridium ljungdahlii, a gram-positive, motile, rod-shaped anaerobic bacterium isolated from chicken waste, has received particular attention for its ability to co-metabolize CO and H_2 to form acetic acid (CH_3COOH) and ethanol (CH_3CH_2OH):

$$4CO + 2H_2O \rightarrow CH_3COOH + 2CO_2 \tag{8.15}$$

$$4H_2 + 2CO_2 \rightarrow CH_3COOH + 2H_2O \tag{8.16}$$

$$6CO + 3H_2O \rightarrow CH_3CH_2OH + 4CO_2 \tag{8.17}$$

$$6H_2 + 2CO_2 \rightarrow CH_3CH_2OH + 3H_2O \tag{8.18}$$

The wild-type strain of *C. ljungdahlii* produced an ethanol-to-acetate ratio of only 0.05 with maximum ethanol concentration of 0.1 g/L. This ratio is very sensitive to acidity; decreasing pH to 4.0 increased the ratio to 3.0. Other adjustments to the culture media and operating conditions nearly eliminated acetate production and increased ethanol concentration to 48 g/L after 25 days.

This gasification/fermentation route to biobased products from lignocellulosic feedstocks has several advantages compared to hydrolytic/fermentation techniques described in Chapter 7. Gasification allows very high conversion of lignocellulosic biomass to usable carbon compounds (over 90%), whereas hydrolysis utilizes only the carbon associated with the carbohydrate (approximately 60% of the total). Gasification yields a uniform product regardless of the biomass feedstock employed, whereas hydrolysis yields a product dependent on the content of cellulose, hemicellulose, and lignin in the feedstock. Finally, since the syngas is produced at high temperatures, gasification yields an inherently aseptic carbon supply for fermentation.

Biological processing of syngas has several advantages compared to chemical processing. The H_2:CO ratio is not critical to biological processing of syngas, thus making unnecessary the water–gas shift reaction to increase the hydrogen content of biomass-derived syngas. Whereas catalytic syngas reactors require high temperatures and pressures, biocatalysts operate near ambient temperature and pressure. Also, biocatalysts are typically more specific than inorganic catalysts.

Syngas fermentation faces several challenges before commercial adoption. Syngas bioreactors exhibit low volumetric productivities due, in part, to low cell densities. Cell recycle and immobilization of cells in bioreactors are possible solutions to this problem. Mass transfer of syngas into the liquid phase is also relatively slow. In commercial-scale aerobic fermentations, mass transfer of oxygen is generally the rate-limiting process. The problem will be exacerbated for syngas fermentations since the molar solubilities of CO and H_2 are only 77% and 65% of that of oxygen, respectively. Possible solutions to this mass transfer limitation are dispersion of syngas into microbubbles of 50 μm diameter and growth of biofilms on gas permeable membranes.

8.4 Fast Pyrolysis

Pyrolysis is the rapid thermal decomposition of organic compounds in the absence of oxygen to produce liquid, gas, and char. The rate of heating, the maximum temperature achieved, the duration of heating, and the manner in which products are cooled strongly influence product distribution. Heating rate is determined by a combination of biomass particle size and physical factors within the reaction environment. Pyrolysis of relatively large pieces of biomass at temperatures around 500°C in a quiescent pile is characterized as slow pyrolysis and produces high yields of char. Pyrolysis of small- to medium-sized pieces of biomass at temperatures above

800°C in a reactor that promotes good gas exchange yields mostly light gases, as described in the section on gasification. Pyrolysis of very small particles ($<$1–3 mm) at temperatures between 300°C and 500°C in reactors that achieve fast heating of biomass and rapid cooling of products is known as fast pyrolysis and produces primarily liquid product. Fast pyrolysis is attractive because the liquid has prospects as heating fuel, a source of chemicals, and feedstock for refining into liquid transportation fuels.

Fast pyrolysis can be thought of as direct liquefaction of biomass although the combination of elevated temperature and relatively modest pressure (often atmospheric) causes any compounds that normally would be liquid at ambient conditions (25°C, 0.1 MPa) to vaporize. The gas stream exiting a fast pyrolyzer contains entrained solid particles of char, noncondensable gases, condensable organic vapors, liquid aerosols, and water vapor. The char consists of carbonaceous residue from the pyrolyzed biomass, mostly elemental carbon, and mineral matter intrinsic (nutrients) or extrinsic (dirt) to the biomass. The noncondensable gases are mostly CO and CO_2 with smaller amounts of H_2 and light alkanes and alkenes. For pyrolysis of lignocellulosic biomass, the condensable organic vapors contain a wide variety of light oxygenated organic compounds, mostly derived from the carbohydrate content of the biomass. Some portion of the condensable organic vapors are phenolic monomers and possibly dimers derived from the lignin in lignocellulosic biomass. The aerosols consist of high-molecular-weight compounds with vapor pressures so low they can only exist in the pyrolysis gas stream as liquid. These include phenolic oligomers derived from lignin and, somewhat surprisingly, sugars or anhydrosugars derived from cellulose and hemicellulose.

Pyrolysis liquid, commonly known as bio-oil, is the combination of condensable vapors, aerosols, and water vapor recovered from the pyrolysis gas stream, yielding between 50 and 75 wt% liquid from lignocellulosic biomass. The recovered bio-oil, as shown in Figure 8.6, is a dark, viscous liquid containing 15–20 wt% water. Bio-oil is best described as an emulsion of lignin-derived phenolic oligomers (sometimes referred to as “water insolubles” or “pyrolytic lignin”) in an aqueous phase composed primarily of carbohydrate-derived compounds. The bio-oil also contains a small amount of suspended char particles carried over in the gas flow to the bio-oil recovery system.

The chemical compositions of bio-oil from softwood (white spruce) and hardwood (poplar) are compared in Table 8.3. The organic phase is listed as “pyrolytic lignin” and is not analyzed for individual components because of its oligomeric nature, but it includes phenolic monomers, dimers, trimers, and tetramers with various functionalities, especially methyl, methoxy, and vinyl. As the result of these reactive phenolic compounds, the organic phase slowly polymerizes during storage, increasing the viscosity and the instability of the emulsion, which may lead to phase separation of the bio-oil. The phenolic oligomers are also responsible for thermal instability of bio-oil when heated during upgrading.

Fig. 8.6 Bio-oil from the fast pyrolysis of lignocellulosic biomass.

The aqueous phase consists mostly of carbohydrate-derived compounds including alcohols, aldehydes, carboxylic acids, esters, furans, pyrans, ketones, monosaccharides, and anhydrosugars, which are responsible for the high oxygen content of the bio-oil. It also contains a small amount of phenolic monomers, which are slightly soluble in water. The bio-oil is highly acidic due to the carboxylic acids, mostly derived from the acetyl group side chains of hemicellulose.

Assuming conversion of 70% of the biomass feedstock to liquid on a weight basis, yields of pyrolysis oil are about 560 L/ton of biomass. The higher heating value of bio-oil ranges between 17 and 20 MJ/kg with liquid densities of about 1280 kg/m^3.

Pyrolysis liquid can be used directly as a substitute for industrial heating oil although it is too corrosive and unstable for commercial or residential applications. In some circumstances, it is also suitable as fuel for combustion turbines or modified diesel engines in stationary power applications. Use as fuel oil substitute is complicated by long ignition delays and varying impacts of water, char, and volatiles content on relative burn rates. The viscosity, density, and surface tension of bio-oil are significantly greater than those of diesel fuel, suggesting that poor atomization might hamper efficient ignition and combustion.

Table 8.3 Analysis of products from fast pyrolysis

	White Spruce	Poplar	Type of Compound
Moisture content, wt%	7.0	3.3	
Particle size, μm (max)	1000	590	
Temperature	500	497	
Apparent residence time	0.65	0.48	
Product yields, wt%, m.f.			
Water	11.6	12.2	
Char	12.2	7.7	
Gas	7.8	10.8	
Pyrolytic liquid	66.5	65.7	
Gas composition, wt%, m.f.			
H_2	0.02	–	
CO	3.82	5.34	
CO_2	3.37	4.78	
CH_4	0.38	0.41	
C_2 hydrocarbons	0.20	0.19	
$C_3{}^+$ hydrocarbons	0.04	0.09	
Pyrolytic liquid composition, wt%, m.f.			
Water-soluble compounds			
Oligosaccharides	–	0.70	Saccharides
Glucose	0.99	0.41	
Other monosaccharides	2.27	1.32	
Levoglucosan	3.96	3.04	Anhydrosugars
1,6-Anhydroglucofuranose	–	2.43	
Cellobiosan	2.49	1.30	
Glyoxal	2.47	2.18	Aldehydes
Methylglyoxal	–	0.65	
Formaldehyde	–	1.16	
Acetaldehyde	–	0.02	
Hydroxyacetaldehyde	7.67	10.03	
Furfural	0.30	–	Furans
Methylfurfural	0.05	–	
Acetol	1.24	1.40	Ketones
Methanol	1.11	0.12	Alcohols
Ethylene glycol	0.89	1.05	
Acetic acid	3.86	5.43	Carboxylic acids
Formic acid	7.15	3.09	
Water soluble—total above	34.5	34.3	
Pyrolytic lignin	20.6	16.2	
Unaccounted	11.4	15.2	
Organic liquid	66.5	65.7	

Source: Piskorz, J., Scott, D.S., and Radlein, D. (1988) *Pyrolysis Oils from Biomass* (eds. E.J. Soltes and T.A. Milne), pp. 167–178. ACS Symposium Series 376. Washington, DC: American Chemical Society.

Bio-oil cannot be used directly as transportation fuel. Like petroleum, it must be refined to molecules compatible with high-performance spark ignition, compression ignition, and gas turbine engines. The diverse composition, low molecular weight, high oxygen content, and high acidity of the aqueous phase and the high viscosity, low volatility, and high reactivity of the organic phase complicate the removal of oxygen (deoxygenation) and refining to fuel-range molecules. The upgrading of bio-oil to transportation fuels is described later in this chapter.

Recovery of high-value chemicals is another possibility, suggesting an integrated approach to production of both chemicals and fuel. For example, levoglucosan is obtained at high yields upon fast pyrolysis of pure cellulose or starch. Even woody or herbaceous biomass can yield significant levoglucosan if metal ions, particularly potassium, are removed or deactivated prior to pyrolysis. Levoglucosan is considered a potential building block for synthesis of dextrin-like polymers, pharmaceuticals, pesticides, and surfactants. Microorganisms have been identified or genetically modified to ferment levoglucosan to citric acid and ethanol, which may be an attractive source of these chemicals if the levoglucosan is obtained from inexpensive lignocellulosic materials. Considering that lignin is both the "glue" that holds together cellulose strands in plant fibers and an antimicrobial agent that protects plant fibers from pests, it is not surprising that phenol has commercial and historical applications in the production of adhesives and antiseptics.

8.4.1 Fundamentals of Pyrolysis

Cellulose, hemicellulose, and lignin have distinctive thermal decomposition behaviors that depend upon heating rate. Under conditions of relatively low heating rate and high ventilation rates with inert sweep gas, hemicellulose is the first constituent to decompose, beginning at 220°C and substantially completing by 315°C. Cellulose does not start to decompose until about 315°C. If volatiles are quickly removed from the reaction zone, cellulose is mostly converted to condensable organic vapors and aerosols once 400°C is attained. High pressures and the absence of ventilation promote char and gas-forming reactions at the expense of condensable organic vapors. Lignin begins to decompose at 160°C but extends to 900°C, yielding a solid residue approaching 40 wt% of the original sample.

Although biomass pyrolysis has traditionally been viewed as random decomposition reactions, recent research is proving that deliberate depolymerization of plant compounds to desired products is possible. For example, scission of the pyranose rings making up the polymeric chains of cellulose and hemicellulose yields mostly light oxygenated compounds like carboxylic acids, aldehydes, ketones, and furans. Experiments on the pyrolysis of pure cellulose, however, reveal that the glycosidic bonds between the rings are preferentially broken, producing predominately 1,6-anhydro-β-D-glucopyranose ($C_6H_{10}O_5$), a singly dehydrated glucose molecule known as levoglucosan. In fact, cellulose is visually observed to melt when exposed to high temperatures. Like sugar, this melted levoglucosan might be expected to polymerize and dehydrate by secondary reactions to form char and light gases. The fact that levoglucosan is found in bio-oil suggests that it is able to escape from the reaction zone before this happens. Some researchers hypothesize that levoglucosan or oligosaccharides are thermally ejected as aerosols out of the pyrolyzer. However, a simpler explanation is that levoglucosan simply evaporates from the pyrolyzer. Whereas most sugars have virtually no vapor pressure, anhydrosugars have measurable vapor pressures at pyrolysis temperatures, allowing them to evaporate before they carbonize. Levoglucosan vapors are relatively stable, allowing them to be transported out of the pyrolysis reactor and recovered. Because levoglucosan can be readily hydrolyzed to glucose, this suggests a pathway for the thermal depolymerization of cellulose to sugars.

The fact that cellulose in the form of lignocellulosic biomass produces only modest amounts of levoglucosan compared to pure cellulose indicates other processes are also occurring. This appears to arise from the naturally occurring alkali and alkaline earth metals (AAEM) found in most biomass, which catalyze ring scission of the pyranose rings in cellulose to yield mostly light oxygenates. The competing processes of glycosidic bond breaking and pyranose ring scission are illustrated in Figure 8.7. Thoroughly washing biomass to remove AAEM prior to pyrolysis dramatically enhances the yield of levoglucosan, but such washing is not a practical operation in large-scale processing. More promising is infusion of small amounts of mineral acid into the biomass, converting the AAEM into thermally stable salts that are no longer effective at catalyzing ring scission, dramatically increasing anhydrosugar production.

Hemicellulose also shows significant thermal depolymerization in the absence of AAEM (see Figure 8.8). Recall that hemicellulose is a large number of het-

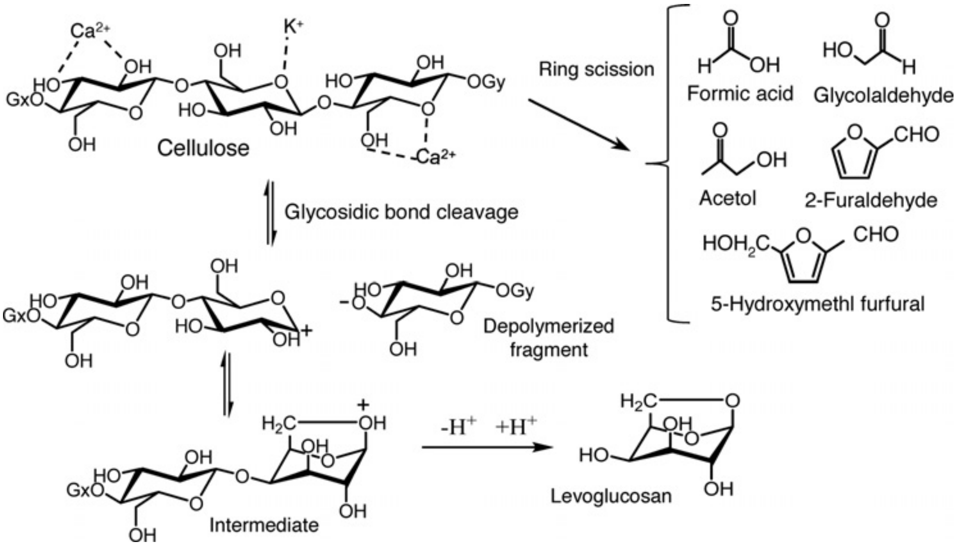
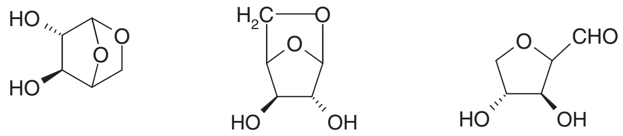


Fig. 8.7 Competing mechanisms of cellulose depolymerization to levoglucosan and alkali/alkaline earth metal catalyzed ring scission to light oxygenated compounds. Adapted from Patwardhan, P.R., Satrio, J.A., Brown, R.C., and Shanks, B.H. (2010) Influence of inorganic salts on the primary pyrolysis products of cellulose. *Bioresource Technology*, 101, 4646–4655.

Anhydroxylopyranoses and anhydroxylofuranose from xylan



1,4-anhydro xylopyranose

1,5-anhydro-beta-D-xylofuranose

2,5-anhydroxylose

Dianhydroxylopyranoses from xylan

5-hydroxy-2H-pyran-4(3H)-one

4-hydroxy-5,6-dihydro-2H-pyran-2-one

(1R,4R)-2,7-dioxabicyclo-[2.2.1]heptan-5-one

(1R,4S)-2,7-dioxabicyclo-[2.2.1]heptan-6-one

Fig. 8.8 Depolymerization and dehydration products from the pyrolysis of pure hemicellulose. Adapted from Patwardhan, P.R., Brown, R.C., and Shanks, B.H. (2011) Product distribution from the fast pyrolysis of hemicellulose. *ChemSusChem*, 5, 636–643.

eropolysaccharides. This discussion will focus on xylan, the predominant hemicellulose in lignocellulosic biomass, which consists of a backbone of β-(1→4)-D-xylopyranose ($C_5H_{10}O_5$) with a variety of side chains. As might be expected, some of the depolymerization products are singly dehydrated xyloses known as anhydroxyloses, including the isomers 1,4-anhydro-xylopyranose; 1,5-anhydro-β-D-xylofuranose; and 2,5-anhydroxylose ($C_5H_8O_4$). Even more prominent are pyrans and tetrahydropyrans, which are dianhydroxylopyranoses (doubly dehydrated xylose), including 5-hydroxy-2*H*-pyran-4(3*H*)-one; 4-hydroxy-5,6-dihydro-2*H*-pyran-2-one; (1*R*,4*R*)-2,7-dioxabicyclo-[2.2.1]heptan-5-one; and (1*R*,4*S*)-2,7-dioxabicyclo-[2.2.1]heptan-6-one. The depolymerization products include significant amounts of acetic acid derived from the acetyl and possibly the 4-*O*-methylglucuronic acid side chains of the xylan.

In the presence of AAEM, these depolymerization/dehydration products are not as prevalent. Instead, products typical of ring scission are evident, including light oxygenates and noncondensable gases like CO_2. Products of severe dehydration reactions are evident including 2-furaldehyde ($C_5H_4O_2$), which is triply dehydrated xylose, and char.

If the polysaccharide in lignocellulose can be converted into anhydrosugars at high yields, this would enhance upgrading of bio-oil to fuels. Anhydrosugars can be hydrolyzed to monosaccharides and fermented to ethanol or butanol. Alternatively, it is more attractive to catalytically upgrade anhydrosugars or sugars (C5–C6) to fuel-range molecules (C5–C22) than to start with light oxygenates (C2–C3).

Lignin, like the polysaccharide in lignocellulosic biomass, also depolymerizes upon rapid heating. Some researchers hypothesize that lignin partially depolymerizes to large fragments that are thermally ejected from the pyrolysis zone, allowing them to be recovered in bio-oil. More consistent with the experimental evidence is depolymerization of lignin to highly substituted phenolic monomers and dimers that are sufficiently volatile to evaporate. The side chains of these phenolic monomers include methyl, methoxy, carboxylic, ethyl, and vinyl groups. Figure 8.9 illustrates some of the substituted phenolic monomers observed as products of pyrolysis. These functionalities impart a wide variety of physical and chemical properties to the phenolic compounds including acidity, boiling point, solubility, and reactivity.

Interestingly, analysis of bio-oil reveals relatively few phenolic monomers and dimers compared to phenolic oligomers in the bio-oil. This is the result of the high reactivity of side chains on the phenolic compounds, which rapidly repolymerize by secondary reactions in the gas phase. The resulting oligomers are no longer volatile, causing them to condense as liquid aerosols, physically evident in the pyrolysis gas stream as light-scattering white smoke. Supporting this theory of

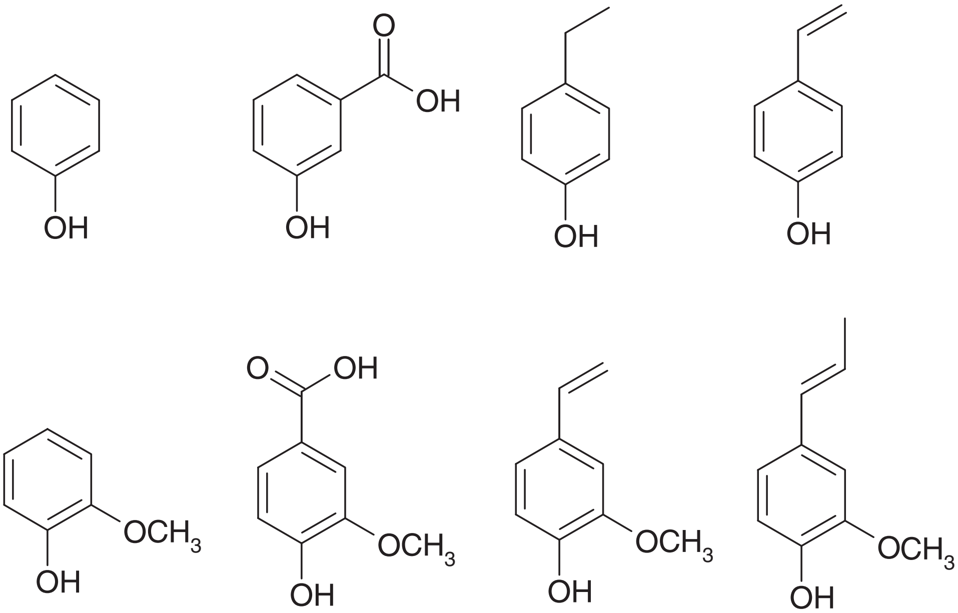


FIG. 8.9 Phenolic monomers from the depolymerization of lignin illustrating methyl (–CH3), methoxy (–OCH3), carboxylic (–COOH), ethyl (–CH2–CH2-) and vinyl (–CH–CH2) functionalities. Adapted from Patwardhan, P.R., Brown, R.C., and Shanks, B.H. (2011) Understanding the fast pyrolysis of lignin. *ChemSusChem*, 4, 1629–1636.

repolymerization in the gas phase is the observation that phenolic oligomers in bio-oil, known as pyrolytic lignin, continue to polymerize at room temperature over the course of hours or even months.

Lignin is the primary source of char during pyrolysis. This is the result of the relatively slow rate of lignin depolymerization to volatile monomers, allowing reactive lignin fragments to repolymerize and subsequently dehydrate to char. As with cellulose, char formation from lignin can be suppressed, although not eliminated, by rapidly heating the biomass and removing the product vapors from the pyrolysis zone.

In principle, lignin-derived molecules are attractive because of their relatively low oxygen content compared to carbohydrates. Phenolic monomers and dimers also have attractive carbon numbers (C6–C20) for production of fuel-range molecules (C5–C22). In practice, many of the lignin-derived compounds in bio-oil are phenolic trimers and tetramers or even larger oligomers. These have viscosities too high and volatilities too low to be easily hydrotreated. Furthermore, their tendency to polymerize and dehydrate when heated also leads to low carbon yields. If the secondary reactions responsible for repolymerization of phenolic monomers could be controlled to produce molecules no larger than dimers, the lignin-derived fraction of bio-oil would be more attractive as refinery feedstock. The secondary reactions of lignin pyrolysis need to be better understood before this possibility is achieved.

8.4.2 Pyrolysis Systems

Pyrolysis systems convert raw biomass feedstock into pyrolysis streams containing noncondensable gases, condensable vapors, aerosols, and char and recover these coproducts as separate streams of solids, one or more liquids, and gases. A wide variety of pyrolysis systems have been developed, which can be categorized as (conventional) fast pyrolysis, catalytic pyrolysis, and hydropyrolysis, as described below. Further classifications are possible based on the method of transferring heat into the reactor and removing products, a description of which is beyond the scope of this introduction to the field.

Fast Pyrolysis

Production of pyrolysis oils and coproducts is illustrated in Figure 8.10. Lignocellulosic feedstock, such as wood or agricultural residues, is milled to fine particles of less than 1 mm diameter to promote rapid reaction, on the order of 1 second. The particles are entrained in an inert gas stream and transported to the pyrolysis reactor. A fluidized bed reactor is illustrated in Figure 8.10 although other kinds of reactors, like auger and entrained flow reactors, can be used as long as they provide the high heat transfer rates and rapid vapor disengagement required for high bio-oil yields. An external source of heat must be supplied to the pyrolysis reactor. Heat exchange can be achieved by either indirect contact (heat transfer

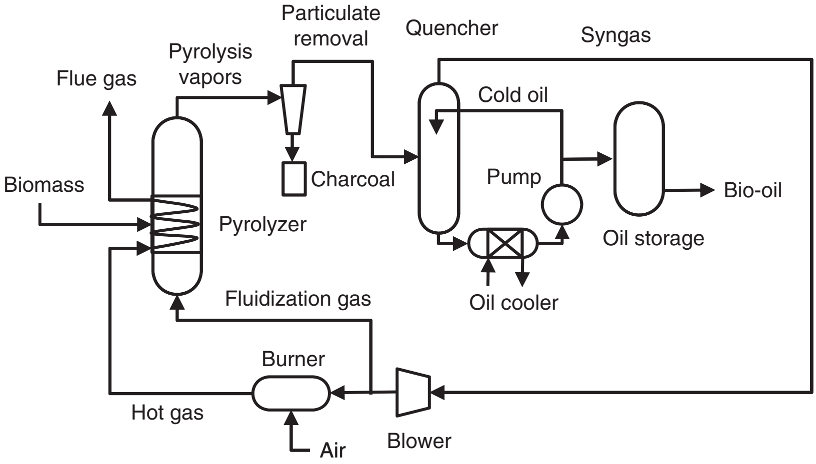


FIG. 8.10 Fast pyrolysis system.

across heat exchange surfaces) or direct contact (circulation of hot sand or steel shot into the pyrolysis reactor). Within the reactor, the particles are rapidly heated and converted into condensable vapors, noncondensable gases, and solid char particles. In fluidized beds and entrained flow reactors, the products are together transported out of the reactor (in auger reactors a large portion of the char is separately removed from the reactor). Those products transported out of the reactor with the pyrolysis gas stream enter a cyclone operating above the condensation temperature of pyrolysis vapors, which allows entrained char particles to be separated.

Vapors and gases are transported to a bio-oil recovery system where they are rapidly cooled to prevent further reaction. Illustrated in Figure 8.10 is a direct-contact quench vessel where a spray of cold pyrolysis liquid cools and condenses the vapors. Other possibilities for bio-oil recovery include arrangements of condensers and electrostatic precipitators to efficiently recover both vapors and aerosols from the pyrolysis stream. The noncondensable gases, which include flammable CO, H_2, and CH_4, are burned in air to provide heat for the pyrolysis reactor. The char is also partly or fully consumed in raising heat for the pyrolyzer.

Bio-oils from such conventional fast pyrolysis systems require extensive deoxygenation to make them suitable as transportation fuel. Alternative pyrolysis processes are described below that partially deoxygenate and otherwise improve the quality of the bio-oil for upgrading to fuels.

Catalytic Pyrolysis

Catalytic pyrolysis uses catalysts either within the pyrolysis reactor (*in situ* catalytic pyrolysis) or immediately downstream of the pyrolysis reactor (*ex situ* catalytic pyrolysis) to promote the formation of desirable fuel precursor molecules. It is distinguished from catalytic upgrading of bio-oil, which occurs after the bio-oil has been recovered as a liquid. Considering the high temperatures and atmospheric pressure commonly employed, catalytic pyrolysis is a vapor phase process, with the catalysts acting on the volatiles released from the pyrolyzing biomass.

Catalysts are able to accelerate desired chemical reactions, breaking and rearranging molecular bonds and adding or subtracting atoms from reactants. Catalyzing reactions before pyrolysis products have condensed to bio-oil has the advantage of processing the primary products of pyrolysis ahead of uncontrolled secondary reactions such as ring scission or repolymerization. Recall also that bio-oil is viscous and nonvolatile, complicating its upgrading, which vapor-phase processing may avoid.

One of the goals of catalytic pyrolysis is to partially or fully deoxygenate carbohydrate-derived compounds through decarbonylation (removal of CO) and decarboxylation (removal of CO_2), at least to the extent of making the product molecules water insoluble (less polar) and less acidic. The less oxygen, water, and acidity the products contain, the more compatible they are with petroleum refining processes. Another goal is to stabilize the phenolic monomers and dimers released from depolymerizing lignin to prevent them from forming large oligomers responsible for the low volatility and high viscosity of conventional bio-oil.

In situ catalytic pyrolysis is attractive because the catalyst is intimately contacted with the pyrolyzing biomass, assuring that primary rather than secondary products of pyrolysis are involved in catalytic reaction. It has the disadvantage that optimal pyrolysis and catalysis conditions may not be achieved in a single reactor. Close contact of minerals or metal salts with the catalyst in the pyrolysis bed may also poison the catalysts and it may be difficult to recover spent catalysts for recycling. *Ex situ* overcomes these disadvantages by separating pyrolysis and catalysis. However, the transport time between the two reactors may allow undesired secondary reactions to occur. Of particular concern is the formation of phenolic oligomers, which are likely to foul *ex situ* catalysts.

Pyrolytic catalysis can be characterized as mild or severe. The goal of mild catalytic pyrolysis is to sufficiently reduce the acidity and polarity of the bio-oil through deoxygenation to allow it to be processed in a petroleum refinery. Severe deoxygenation attempts to produce hydrocarbon molecules. An example of severe catalytic pyrolysis uses acidic zeolite catalysts to crack and dehydrate carbohydrate to aromatic hydrocarbons, including benzene, toluene, and xylene (BTX), which are high-value petrochemicals and octane boosters for gasoline. Although aromatic yields are as much as 17 wt%, coke yields are unattractively high at present. Catalytic pyrolysis does not use hydrogen or other gaseous reducing agents in part because of the difficulty of operating reactors that process solid fuels at the high pressures thought important for these reducing agents to be effective.

Hydropyrolysis

Hydropyrolysis pyrolyzes biomass in the presence of both catalyst and high-pressure hydrogen to produce highly deoxygenated molecules, often hydrocarbons. Although not well understood, the addition of high-pressure hydrogen to a pyrolysis reactor in the presence of a catalyst probably accomplishes both hydrodeoxygenation of pyrolysis vapors and stabilization of lignin-derived phenolic compounds, preventing them from forming high-molecular-weight oligomers that would require even more severe reactions conditions to crack into fuel-range molecules. The advantage of hydropyrolysis over catalytic pyrolysis is carbon yield. Although, like catalytic pyrolysis, some coke is formed, oxygen is removed as water rather than as carbon monoxide and carbon dioxide, preserving more carbon in the fuel products. The disadvantage is operation at high pressure, up to 5 MPa, which makes difficult the continuous feeding of biomass into the pyrolyzer. Although the products are very attractive from the standpoint of refining into fuels, further development of pressurized feeding systems for solid biomass is required to make this process feasible.

8.5 Solvolysis

Solvolysis in the most general sense is the interaction of a solvent with a solid or liquid reactant to produce chemical products. Although the reference to solvent suggests that the reactant and/or products are dissolved in the solvent, this is not necessarily the case. Sometimes both solvent and reactant participate in the chemical reaction, but in other cases the solvent merely serves as heat or mass transfer medium. Solvolysis often involves the thermal decomposition of complex organic compounds, in which case it can be thought of as "pyrolysis in a solvent," although specific reactions and products can be quite different for pyrolysis and solvolysis.

Both polar and nonpolar solvents can be used. Among polar solvents, both protic and aprotic solvents have application (protic solvents can participate in hydrogen bonding or even donate hydrogen to the reaction). When water is used as solvent, especially convenient when processing high-moisture feedstocks, solvolysis is referred to as hydrothermal processing. Sometimes mixtures of solvents are used, frequently to produce a biphasic system of polar and nonpolar phases to improve product separation and recovery. Both homogeneous (liquid) and heterogeneous (solid) catalysts have been explored to enhance yields and improve product selectivity.

Like some other thermochemical conversion technologies, solvolysis was originally developed to convert (solid) coal into liquid fuels. This coal-to-liquid process is referred to as direct liquefaction, in contrast to indirect liquefaction achieved by first gasifying coal and then catalytically synthesizing liquid fuels from the gas. The term "solvent liquefaction" has also been applied, but more generally, solvolysis can produce solids and gases as well as liquid products.

Solvolysis is attractive for the wide range of products that can be produced from a given feedstock by controlling the processing conditions, including the choice of solvent. Bio-oil from solvolysis usually has lower oxygen and water content than bio-oil from pyrolysis; therefore, it has some advantages in upgrading to transportation fuels. Solvolysis requires further development before it becomes commercially significant. First is the need to continuously process solid biomass at elevated pressures, which prevents solvent from evaporating during reaction. Pressures can be as high as 18 MPa for systems using water and operating at 350°C. The second disadvantage is the cost of nonaqueous solvents, which are expensive to use unless they are efficiently recovered and reused or generated by the process.

8.5.1 Direct Liquefaction of Lignocellulose

Direct liquefaction was first developed in Germany during the 1910s to convert coal into liquid hydrocarbons. Although the original patents claimed the process was applicable to a wide variety of solid carbonaceous feedstocks, there is no evidence that biomass was ever evaluated in a continuous process. Direct liquefaction of coal, on the other hand, was put into commercial practice in Germany during World War II when the country was denied access to petroleum resources.

Known as the Bergius process after its inventor, direct liquefaction was accomplished by slurring coal with a tarry solvent and reacting the mixture with hydrogen over a metal catalyst at 490°C and 23 MPa. The solvent promoted heat and mass transfer and shuttled hydrogen from the gas phase to the coal. The high temperature thermally ruptured carbon–carbon bonds, allowing hydrogen to react with the coal, increasing the H:C ratio required to produce liquid hydrocarbons. Operation at high pressure prevented evaporation of solvent and increased the partial pressure of hydrogen, which promoted reaction. The liquid, produced in yields of 40–60 wt%, was separated into a "middle distillate" that was further hydrogenated to produce gasoline-range molecules and "still bottoms" that were used as make-up solvent.

Efforts to directly liquefy biomass did not emerge until the 1970s, apparently inspired by the original Bergius process. Biomass mixed with hydrocarbon solvent is reacted with various catalysts at temperatures ranging from 230°C to 450°C and pressures from 7 to 50 MPa. When solvent serves as hydrogen donor, it is primarily to reduce the O:C ratio of the biomass-derived products rather than to increase its H:C ratio. Both hydrogen and carbon monoxide gases have been tested as reducing agents with the notion that biomass-derived producer gas might be used to deoxygenate the biomass. Oxygen could also be removed through decarbonation or decarboxylation of the biomass without the addition of an external reducing agent.

In contrast to the single-phase liquid product produced from coal, direct liquefaction of lignocellulosic biomass yields two distinct phases of liquid product: a phenolic-rich, water-insoluble organic phase derived primarily from lignin and an aqueous phase derived mostly from carbohydrate and containing up to 30% of the original energy of the biomass. The organic phase, sometimes referred to as bio-oil, is partially deoxygenated and has lower moisture and higher heating value than pyrolysis-derived bio-oil. Differences between the two kinds of bio-oil are partly due to deoxygenation achieved by solvolysis, but they also reflect the presence of water in the pyrolysis-generated bio-oil. Direct liquefaction can produce a wide range of liquid products, including aliphatic and aromatic alcohols, phenols, hydrocarbons, substituted furans, and alicyclic compounds. Like coal-derived oil, the organic phase can be upgraded by reaction with high-pressure hydrogen in the presence of a catalyst, a process known as hydroprocessing.

8.5.2 Hydrothermal Processing of Lignocellulosic Biomass

Hydrothermal processing exploits enhanced solvent properties of compressed or supercritical water. Many organic nonpolar compounds become miscible with water under such condition, and the presence of H_3O^+ and OH^- ions in pressurized water serve as acid and base catalysts in the media. Hydrothermal processing of wet lignocellulose can produce extracted biomass components, fractionated biomass components, liquefied biomass, or gasified biomass depending upon the reaction conditions, often without catalysts (see Figure 8.11). As reaction temperature increases, higher pressures are required to prevent boiling of the water in the wet biomass.

At temperatures around 100°C, extraction of high-value plant chemicals such as resins, fats, phenolics, and phytosterols is possible. At 200°C and 2 MPa, fibrous biomass undergoes a fractionation process to yield cellulose, hemicellulose degradation products such as furfural or 5-hydroxy-methylfurfural (HMF), and lignin. Further hydrothermal processing can hydrolyze the cellulose to glucose. At 300–350°C and 12–18 MPa, biomass undergoes more extensive chemical reactions yielding a water-insoluble organic phase known as (hydrothermal processing) bio-oil. Although superficially resembling bio-oil from pyrolysis, it has lower oxygen content and is less miscible in water, making it more amenable to hydroprocessing. At 600–650°C and 30 MPa, the primary reaction product is gas, including a significant fraction of methane.

Continuous feeding of biomass slurries into high-pressure reactors and efficient energy integration represent engineering challenges that must be overcome before HTP results in a commercially viable technology.

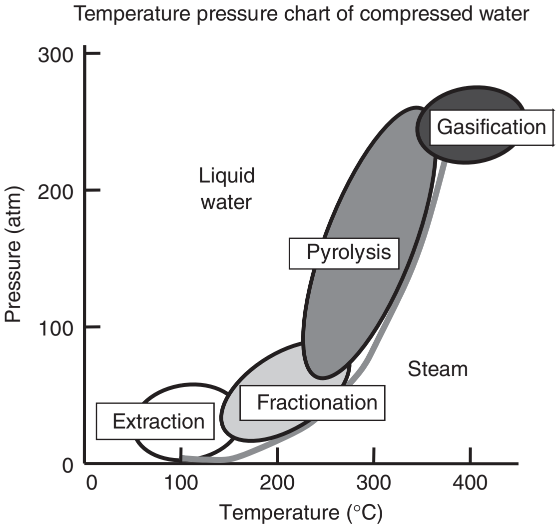


FIG. 8.11 Different operating regimes for hydrothermal processing: extraction, fractionation, pyrolysis, and gasification.

8.6 Chemical Upgrading to Transportation Fuels

Thermochemical or biochemical processing of herbaceous or woody biomass produces "deconstructed lignocellulosic biomass" that requires further processing to finished products. Deconstructed lignocellulosic biomass includes sugars or solubilized carbohydrate liberated from lignocellulosic biomass by acid or enzymatic hydrolysis or thermal depolymerization; and bio-oil from fast pyrolysis or solvolysis. They may exist as an emulsion of water-insoluble organic phase in an aqueous phase or separate phases of water-insoluble organics and aqueous solutions of soluble organic compounds. Usually the liquids contain significant oxygen although partial deoxygenation may have occurred in producing the deconstructed lignocellulosic biomass. The goal of chemical upgrading is to convert these feedstocks into either commodity chemicals and finished fuels or blendstocks suitable for additional upgrading in a conventional petroleum refinery. In that respect, deconstructed lignocellulose may be thought of as “bio-crude.”

Early in the development of pyrolysis and solvolysis, it was hoped that upgrading technologies developed over 100 years of petroleum refining could be used to upgrade bio-oils into finished fuels. However, there are important differences between unrefined petroleum, also known as crude oil, and deconstructed lignocellulosic biomass that prevents a simple translation of upgrading technologies. Unrefined petroleum is a mixture of mostly alkane and aromatic hydrocarbons containing few functional groups. As a result of this chemical composition, unrefined petroleum is nonpolar, contains only a small amount of unstable compounds, and is relatively volatile. The petroleum industry exploits these properties in refining petroleum to fuels. Crude oil often contains water, salts, and insoluble minerals, which need to be removed before processing. Because petroleum is nonpolar and water is polar, they are immiscible in one another allowing water to be used to wash salts and other minerals out of the petroleum, followed by simple phase separation to remove the water. Because petroleum is relatively stable and volatile, it can be heated and separated into hydrocarbon fractions according to boiling point, which can be upgraded by the well-established refining processes.

Deconstructed lignocellulosic biomass, on the other hand, is a mixture of sugars and light oxygenates derived from carbohydrate- and lignin-derived aromatic compounds. The carbohydrate-derived compounds are polar and include diverse oxygen-rich functionalities. With the exception of anhydrosugars, saccharides have virtually no volatility. The lignin-derived compounds are aromatic but contain significant functionalities and often exist as nonvolatile, highly reactive oligomers. Deconstructed biomass often contains significant water, which readily dissolves the polar, carbohydrate-derived compounds, making it impossible to remove water and dissolved minerals before upgrading. The lack of volatility and high reactivity of many of the constituents makes impossible fractional distillation. Often the only separation that is achieved is an aqueous phase containing mostly carbohydrate-derived compounds and an organic phase containing mostly lignin-derived compounds. The deconstructed biomass contains considerably more oxygen than does petroleum, which must be substantially removed if hydrocarbon fuels are desired.

8.6.1 Chemical Upgrading from the Perspective of Petroleum Refining

Differences between deconstructed lignocellulosic biomass and petroleum preclude its direct substitution into a conventional petroleum refinery. However, the basic refining processes of *cracking*, *treating*, *reforming*, *combining*, *and reshaping* still have relevance to upgrading of deconstructed biomass. Reactions in the presence of hydrogen, collectively referred to as *hydroprocessing*, are especially relevant because of their ability to deoxygenate biomass at high carbon utilization efficiencies. These include hydrotreating and hydrocracking. *Steam reforming* is also extremely important for its ability to generate the hydrogen required for hydroprocessing.

Basic refining processes are described in the following sections in terms of the kinds of chemical reactions that occur. These include *elimination reactions*, *substitution reactions*, *addition reactions*, *and rearrangement reactions* (refer to Chapter 3).

Cracking

Cracking, as defined in the petroleum industry, is *elimination reactions* that break the very large molecules of heavy gas oil (230–425°C boiling point) or distillation residual (>425°C boiling point) into lower boiling point molecules that are more easily upgraded to fuels in subsequent refining processes. Several kinds of crackers have been developed, classified as thermal crackers, catalytic crackers, or hydrocrackers.

Thermal crackers use high temperatures around 500°C to promote rapid decomposition of large molecules without the aid of catalyst or the addition of hydrogen. *Elimination reactions* of these large molecules are accompanied by scission of carbon–carbon bonds and formation of carbon–hydrogen bonds, which results in a deficit of hydrogen and the formation of elemental solid carbon, known as coke. Addition of steam can reduce "coking," but not eliminate it. Furthermore, the reaction of steam and coke simply produces light gases rather than fuel-range molecules.

Catalytic cracking produces higher yields of fuel-range molecules, but there is still a deficit of hydrogen and coke deposits on the catalyst, eventually deactivating it. In a process known as fluid catalytic cracking (FCC), the catalyst is continuously circulated from the cracking reactor to a catalyst regenerator that burns off the coke and returns it to the cracking reactor. Interestingly, catalytic cracking with a zeolite catalyst is effective in deoxygenating deconstructed plant carbohydrates through the elimination reactions of decarbonylation (CO removal) and decarboxylation reactions (CO_2).

Hydrocracking is catalytic cracking in the presence of hydrogen, which allows more hydrocarbons and less coke to form. Hydrocracking would be particular effective in producing deoxygenated, fuel-range molecules from the phenolic oligomers in bio-oil. Although more carbon efficient than thermal or catalytic cracking, hydrocracking has the disadvantage of needing an external source of hydrogen, which adds to the expense of the process.

Treating

Treating has the goal of removing objectionable elements from the feedstock and stabilizing it for subsequent refining steps. The elements in question include nitrogen, sulfur, chlorine, and oxygen. They occur as both heteroatoms in carbon rings and as part of functional groups. They do not exceed more than a few weight percent in unrefined petroleum. Deconstructed lignocellulosic biomass also contains these elements but usually in smaller concentrations with the prominent exception of oxygen, which may represent 50 wt% of the dry feedstock. These elements are undesirable in the upgrading of feedstocks to hydrocarbon fuels, commonly interfering with catalytic upgrading or generating pollutant emissions when burned. In large concentrations, oxygen reduces the energy density and increases the molecular polarity of the fuel compared to hydrocarbons, which complicates their blending with petroleum-derived fuels.

Stabilization of the feedstock involves transforming particularly reactive molecules into forms more amenable to additional processing. In the case of petroleum, the problematic hydrocarbons are the double carbon bonds of alkenes (also known as olefins), which can oligomerize in an undesired manner. In the case of deconstructed biomass, the functionality associated with aldehydes and carboxylic acids derived from carbohydrate and methoxy and vinyl substituents on phenolic compounds derived from lignin are thought to contribute to feedstock instability.

In a process known as hydrotreating in the petroleum industry, *substitution reactions* under relatively mild catalytic conditions replace sulfur, nitrogen, chlorine, and oxygen in the feedstock with hydrogen, yielding the respective byproducts hydrogen sulfide (H_2S), ammonia (NH_3), hydrochloric acid (HCl), and water (H_2O). Hydrotreating furthermore removes metal contaminants, which react with chlorine to form easily removed metal chlorides. *Addition reactions* of hydrogen also occur during hydrotreating of petroleum, saturating the double carbon bonds of alkenes in a process known as hydrogenation, improving the stability of the petroleum.

Applied to deconstructed biomass, hydrotreating removes nitrogen, sulfur, chlorine, and metals. It also hydrogenates vinyl functional groups. It would also partially deoxygenate the feedstock through *substitution reactions* with functional groups, but the reaction conditions are sufficiently mild that only the most reactive functional groups would be removed. More severe reaction conditions are required to completely deoxygenate the deconstructed biomass, such as previously described cracking.

Reforming

Reforming consists of a variety of *elimination reactions* that remove molecular hydrogen from hydrocarbons or other organic compounds. It may be thought of as the reverse of hydrogenation although reforming reactions can be more involved than simply producing unsaturated carbon–carbon bonds. Under high-temperature reforming conditions in the presence of steam, the ultimate products of reforming are CO and H_2, a circumstance that is exploited to convert natural gas or other sources of simple organic compounds into syngas. High-temperature reforming may be accomplished without a catalyst although catalysts are frequently employed for lower temperature reforming.

In the petroleum industry a process called catalytic reforming is employed to convert naphtha from the distillation of petroleum (220–315°C boiling point range) into gasoline molecules (90–220°C boiling point range). Among the most important reactions in catalytic reformers are *elimination reactions* that either convert alkanes (paraffins) into cycloalkanes (naphthenes) and hydrogen or cycloalkanes into aromatics and hydrogen. Not only are the hydrocarbon products higher octane fuel molecules than the reactants, the hydrogen is useful for hydrotreating and hydrocracking.

Catalytic reforming as practiced by the petroleum industry has little relevance to refining deconstructed biomass because it contains few hydrogen-rich molecules in the naphtha range. On the other hand, steam reforming light oxygenates (C_2–C_3) derived from carbohydrate, which would be difficult to upgrade into fuel-range molecules, produce large quantities of hydrogen for hydroprocessing.

Combining

Combining is *addition reactions* that convert two molecules into a single larger molecule. This is highly desirable from the standpoint of producing liquid fuels from biomass-derived molecules that otherwise are too volatile (C_2–C_4) to be used for fuel. A prominent example of addition reactions in petroleum refining is alkylation of isobutene (C_4H_{10}) with propene (C_3H_6) or butene (C_4H_8) to produce isoheptane (C_7H_{16}) and isooctane (C_8H_{18}), respectively, both important as gasoline-range molecules. *Addition reactions* also include polymerization (or more correctly oligomerization), which is the compounding of monomers into hydrocarbon chains. For example, the low-boiling point olefin monomers of propene and butene can undergo additive polymerization to produce high-octane, gasoline-range molecules known as polymer gasoline. Of course, if oligomerization proceeds too far, the molecular weights become too high for fuel applications (due to high viscosity and low volatility). Although deconstructed biomass is not rich in olefins, it contains other compounds that can easily polymerize, such as the phenolic monomers produced from lignin, but this usually occurs in an uncontrolled manner, producing molecules too large to use as transportation fuels.

Reshaping

Reshaping, or isomerization, is the rearrangement of chemical bonds among the constituents of a molecule to produce a molecule with the same chemical formula but distinctive chemical and physical properties. Isomerization is important in increasing the octane rating of fuels, especially by converting normal (straight-chain) alkanes into iso-alkanes (containing branched chains). In petroleum refining, some isomerization occurs in catalytic reformers. Dedicated isomerization plants are also built to produce feedstocks for alkylation plants and to improve the octane rating of straight-chain pentane and hexane. Isomerization would likely be important in a mature advanced biofuels industry. Currently the focus is on deoxygenating biomass-derived molecules into fuel-range hydrocarbons suitable for blending with petroleum-derived fuels rather than optimizing octane or cetane numbers.

8.6.2 Upgrading Deconstructed Lignocellulosic Biomass

The field of upgrading deconstructed lignocellulosic biomass into fuels is still developing, but some general strategies are emerging. Bio-oil from pyrolysis and solvolysis would likely be upgraded in a similar manner, despite some important differences between them. The bio-oil from solvolysis consists of only the water-insoluble organic phase of the solvolysis products in contrast to bio-oil from pyrolysis, which is an emulsion of the water-insoluble organic phase in the aqueous phase. Solvolysis apparently deoxygenates biomass sufficiently to cause phase separation into separate water-insoluble and aqueous phases. Bio-oil can also be recovered as separate insoluble and aqueous phases, either by addition of water to the bio-oil or through the use of fractionating recovery processes during pyrolysis. In either case it appears that the water-insoluble phase is derived substantially from lignin while the aqueous phase is derived from the carbohydrate.

Early attempts to upgrade bio-oil focused on hydroprocessing to simultaneously remove oxygen and crack the large phenolic oligomers. The high temperatures employed quickly caused unstable functional groups, probably carbonyl in the carbohydrate-derived compounds and vinyl groups on phenolic compounds, to foul the catalysts with coke. Since then it has been discovered that mild hydrotreating of the bio-oil improves the stability of the bio-oil without substantially deoxygenating it. A second, more severe stage of hydrotreating then deoxygenates especially the light carbohydrate compounds, producing a product stream of light hydrocarbon oil, heavy phenolic oil, and light hydrocarbon gases. After separating these streams, the heavy phenolic oil is hydrocracked, which both reduces the phenolic oligomers to fuel-range molecules and deoxygenates functional groups and hydrogenates some of the aromatic rings. In principle, the heavy phenolic oil could be catalytically cracked, which would reduce hydrogen demand, but current zeolite catalysts do not appear efficient at cracking this material. The products of hydroprocessing are recovered as gasoline- and diesel-range molecules and light hydrocarbon gases that can be steam reformed to produce part of the hydrogen required for hydroprocessing with the balance coming from natural gas reforming. The overall process for upgrading whole bio-oil is illustrated in Figure 8.12a.

There are two major problems with upgrading whole bio-oil. First, not enough light hydrocarbon gases are generated to supply hydrogen via steam reforming. Natural gas is a relatively inexpensive source to supply the hydrogen deficit, but it is a fossil fuel and generates net greenhouse gas emissions. This deficit in hydrogen arises from the highly oxygenated nature of the aqueous phase of the bio-oil compared to the organic phase. Second, much of the organic content of the aqueous phase consists of C_2- and C_3-oxygenated molecules that consume significant hydrogen to deoxygenate them but yield molecules too small to be used in gasoline. They are simply recycled to the steam reformer, which represents inefficient uses of energy and hydrogen. A solution to these problems is illustrated in Figure 8.12b. The bio-oil is separated into water-insoluble organic phase and aqueous phase with the former upgraded through one or two stages of hydrotreating and one stage of hydrocracking, while the aqueous phase is steam reformed to hydrogen. The amount of hydrogen generated in this manner is more than required to upgrade the organic phase, thus avoiding the use of fossil fuels to produce the

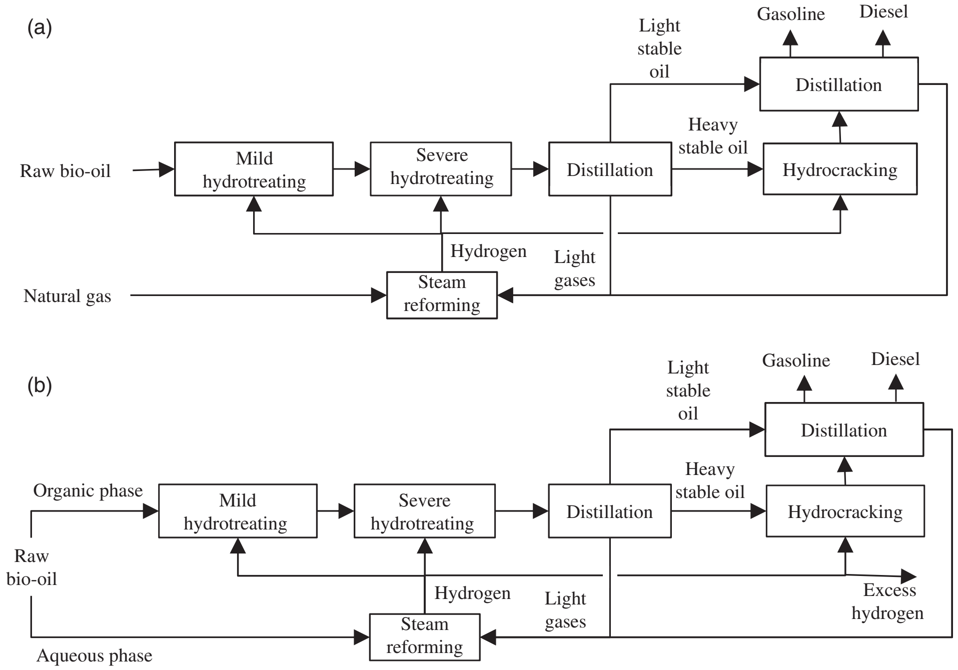


FIG. 8.12 Upgrading of pyrolysis liquids (a) hydroprocessing whole bio-oil; (b) hydroprocessing organic phase (aqueous phase steam reformed to hydrogen). Adapted from Jones, S.B., Valkenburg, C., Walton, C.W., et al. (2009) Production of gasoline and diesel from biomass via fast pyrolysis, hydrotreating and hydrocracking: a design case. *PNNL Report PNNL-18284*.

fuel. The process is not as carbon efficient in converting biomass to biofuels as upgrading whole bio-oil, but it has significantly lower greenhouse gas emissions.

Other approaches to improving the utilization of the aqueous phase for biofuels production is to increase the amount of carbohydrate converted to sugars or anhydrosugars, which would produce C_5 and C_6 hydrocarbons upon catalytic upgrading. This possibility was discussed in the section on pyrolysis. Another approach is to identify catalytic processes that build fuel-range molecules from C_2–C_4 molecules through *addition reactions* or *condensation reactions*. Various alkylation and aldol condensation reactions in combination with ketonization and dehydration reactions are being developed to convert these small molecules into C_7–C_{15} fuel molecules.

Further Reading

Combustion

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