

Products from Biorenewable Resources

6.1 Introduction

Biorenewable resources can be converted into bioenergy or biobased products. *Bioenergy* includes process heat, biopower, and biofuels; while *biobased products* include chemicals and natural fibers, from which an array of finished products can be manufactured. This chapter is an introduction to these products from biorenewable resources and gives some idea of their use in commercial markets.

Process heat is the thermal energy used to raise the temperature of solids, liquids, or gases for residential, commercial, or industrial applications. It includes heating of homes, firing of bakery ovens, heating water for laundries, drying grain, raising steam for manufacturing processes, melting ores, and a variety of other low- and high-temperature processes. Other than a few instances of solar and geothermal heating, almost all process heat is derived from combustion in air of energy-rich organic compounds like coal, natural gas, or biomass, collectively referred to as fuels. Combustion generally occurs at very high temperatures, which for many applications must be moderated by post-combustion dilution of the resulting flue gas or heat transfer to water or other media.

Biopower is defined as the conversion of biorenewable resources into electric power. It is usually intended to designate energy for stationary applications as opposed to energy for transportation. This distinction is important, as biopower applications typically employ solid or gaseous fuels, whereas transportation applications employ liquid fuels, although there are exceptions to these generalizations.

Biofuels are chemicals derived from biorenewable resources that have sufficient volumetric energy densities (enthalpies of reaction per unit volume) and combustion characteristics to make them suitable for transportation applications. Generally, transportation fuels are confined to liquids including hydrocarbons, alcohols, and esters that are readily vaporized and burned within heat engines.

Hydrogen may eventually be classified as a practical transportation fuel if gas storage technologies can substantially improve over present storage methods based on metal hydrides and high-pressure tanks. Wood and other solid biomass, despite respectable energy densities, do not have handling and combustion characteristics suitable for transportation fuels. The literature often fails to distinguish between *fuels*, which are any substances that can be burned for the production of heat or power, and *transportation fuels*, which is a distinct subset of fuels. The distinction is important because of the more exacting specifications required for transportation fuels.

Chemicals usually are taken to be commodity chemicals, such as acetic acid and propylene glycol, although it can include fine chemicals such as proteins and pharmaceutical chemicals. Commodity chemicals find applications in the manufacture of a wide variety of products including absorbents, adhesives, solvents, lubricants, inks, pesticides, coatings, films, and polymers. Some chemicals, such as ethanol, can be classified as either chemical or transportation fuel, depending upon its ultimate application.

Natural fibers are the elongated cells in the tissues of vascular plants that serve a structural function. Very long, fine fibers such as cotton are used in the manufacture of cloth, while wood fiber is the source of pulp in papermaking. Clearly, polymers synthesized from biorenewable resources can be spun into fibers, but these are synthetic fibers. In this book, fibers separated from biorenewable resources are classified as natural fibers, whereas fibers spun from polymers that have been synthesized from biorenewable resources are classified as synthetic fibers.

The following sections describe the application and potential markets for products from biorenewable resources. In the case of process heat and biopower, this involves a description of the equipment used to convert thermal energy or gaseous fuel generated from biomass into heat and power. The section on biofuels describes issues related to the satisfactory use of liquid fuels derived from biorenewable resources in transportation applications. The section on chemicals will introduce the reader to commodity chemicals in today's markets and indicate where chemicals from biorenewable resources might find market entry. Finally, the section on fibers will explain how natural fibers, once separated from plant materials, can be manipulated into biobased products.

6.2 Process Heat

Oxidation of carbon–carbon and carbon–hydrogen bonds in carbohydrates, lipids, and protein are exothermic reactions. Thus, sufficiently dried, any biorenewable resource can be burned as a source of thermal energy. In practice, sugars, starches, lipids, and proteins are too valuable in the production of food, transportation fuels, and chemicals to be burned for heat or even power. Only lignocellulosic materials,

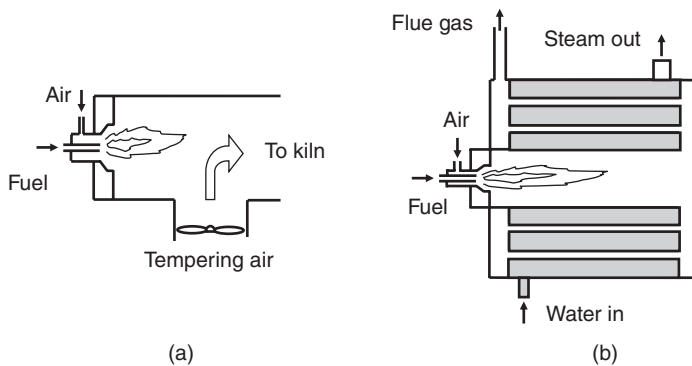


FIG. 6.1 Examples of process heaters: (a) direct-fired burner for a kiln; (b) indirect-fired water-tube boiler.

such as wood and straw, and mixed waste streams, like manure or municipal solid wastes, are likely candidates for process heat, either by directly burning them as solid fuel or after processing them to flammable gases or liquids (see Chapter 8).

Process heat may be required at temperatures as low as 30°C , for example, in heating an anaerobic digester, or as high as 2500°C , for example, in calcining limestone for the production of concrete. Fired process equipment, also known as a *furnace*, is used to burn fuel and deliver process heat at a desired temperature. As illustrated in Figure 6.1, process heaters can be either directly fired or indirectly fired.

6.2.1 Direct-Fired Furnaces

Direct-fired furnaces either burn fuel directly in the process stream or the flue gas from combustion is brought into contact with the process stream. The most common examples of direct-fired furnaces are grain driers, wood kilns, cement kilns, and metal forging ovens. As illustrated in Figure 6.1a, temperature control is achieved by adding air in excess of what is required to burn the fuel. Direct firing has the disadvantage of potentially introducing contaminants from the flue gas stream into the process stream. Although flue gas from the combustion of biomass is primarily a mixture of nitrogen, carbon dioxide, water vapor, and lesser amounts of oxygen, it also contains traces of alkali metals (sodium and potassium), acid gases (hydrogen chloride, sulfur dioxide, and nitrogen oxides), and tar, which is a mixture of oxygenated organic compounds. Modern standards of quality control preclude direct-fired furnaces fueled by biomass except in a few circumstances, such as wood drying or calcining of limestone. On the other hand, if the biomass is first converted to flammable gases, by either thermal gasification or anaerobic digestion, followed by a gas-cleaning step, the resulting gases may be suitable for

use in direct-fired furnaces. However, gas cleaning results in additional capital cost. This cleaning step may be justified for advanced power generation, as subsequently described, but may not be economical for process heat applications.

6.2.2 Indirect-Fired Furnaces

Indirect-fired furnaces do not allow the products of combustion to come in direct contact with the process stream. When very high temperature process heat is required, the combustion stream is separated from the process stream by a thermally conducting wall. Such *process heaters* are commonly used for cracking hydrocarbons or as reboilers in distillation of heavy petroleum liquids.

Another approach to indirect-fired furnaces is to employ a heat-transfer media to move thermal energy from the combustion stream to the process stream. *Air-to-air heat exchangers* have been successfully used in conjunction with biomass combustors to transfer heat from hot, dirty flue gas to a clean air stream. The relatively low convection coefficients associated with gas, however, result in large heat exchangers. *Thermal fluid heaters* are employed in applications where high-pressure steam is to be avoided as heat transfer media. Suitable thermal fluids include water for relatively low temperature applications (100–250°C) and low vapor pressure organic liquids for moderate temperature applications (250–400°C). *Boilers* use steam as a clean, non-corrosive, high-energy content heat transfer media capable of operating at moderately high temperatures (200–540°C). The steam generated is suitable for either direct-contact or indirect-contact heat exchange with process streams.

A *fire-tube boiler*, illustrated in Figure 6.1b, consists of a large, cylindrical shell containing water to be converted to steam. Through the center of this vessel passes a large diameter “fire tube” where combustion of the fuel occurs. The flue gas produced exits through a bundle of smaller tubes surrounding the central fire tube. These boilers are most suited for gaseous or volatile liquid fuels. *Water-tube boilers* consist of a large chamber or firebox that is either penetrated or surrounded by small-diameter tubes containing water. Fuel is burned in the firebox at high temperatures with heat transmitted to the steam tubes by radiation from the flame and by convection from the hot flue gases. Water-tube boilers are the most appropriate technology for direct combustion of biomass fuels. Raising steam from biomass fuels is examined in Chapter 8.

6.3 Biopower

A variety of thermodynamic cycles have been devised to convert heat into work. Power cycles of relevance to biopower include the Stirling, Otto, Diesel, Rankine, and Brayton cycles. From a theoretical perspective, the thermodynamic efficiencies

of all five of these cycles are limited by the Carnot efficiency, which states that the maximum efficiency η_{\max} of a heat engine is a function of the temperatures at which the engine receives heat from a high temperature T_H and rejects heat to a low temperature T_L .

$$\eta_{\max} = 1 - \frac{T_L}{T_H} \quad (6.1)$$

Accordingly, heat engines must operate at temperatures as high as can be tolerated by the materials of construction in order to achieve the maximum conversion of chemical energy into work. This limit, along with various irreversibilities such as friction, turbulence, and heat transfer, restricts thermodynamic efficiencies of practical heat engines to the range of 35–50%.

6.3.1 Stirling Cycle

The Stirling cycle is an example of an external combustion engine; that is, the products of combustion do not come into contact with the fluid that undergoes the thermodynamic processes of the cycle. In this respect, it resembles the Rankine steam cycle although its thermodynamic efficiency is theoretically higher than that of the Rankine cycle operating on the same fuel. In practice, the efficiencies of Stirling engines are relatively modest as are their output power, typically no more than a few kilowatts. They continue to attract attention mainly because of their low maintenance, high tolerance to contaminants, and relatively low pollution emissions. However, high costs have prevented significant market entry.

6.3.2 Otto and Diesel Cycles

Internal combustion engines are the practical manifestations of the Otto and Diesel cycles. They are robust in operation, efficient at small scales, and are more tolerant of contaminants than are gas turbines. Nevertheless, they are generally confined to niche markets for stationary power applications. Probably, the most important reason for this situation is a limit on their size, which is on the order of 5 MW. Economies of scale, which indicates that the cost of a product goes down as the production facility gets larger, has led the electric utility industry to build power plants that typically produce hundreds if not thousands of megawatts of electricity. Internal combustion engines cannot compete in this arena. Even at the scale of hundreds of kilowatts, internal combustion engines may not be attractive for future biopower applications because of their relatively high pollution emissions and limited opportunities to enhance their efficiency. Application of internal combustion engines for vehicular propulsion is discussed in the section on transportation fuels.

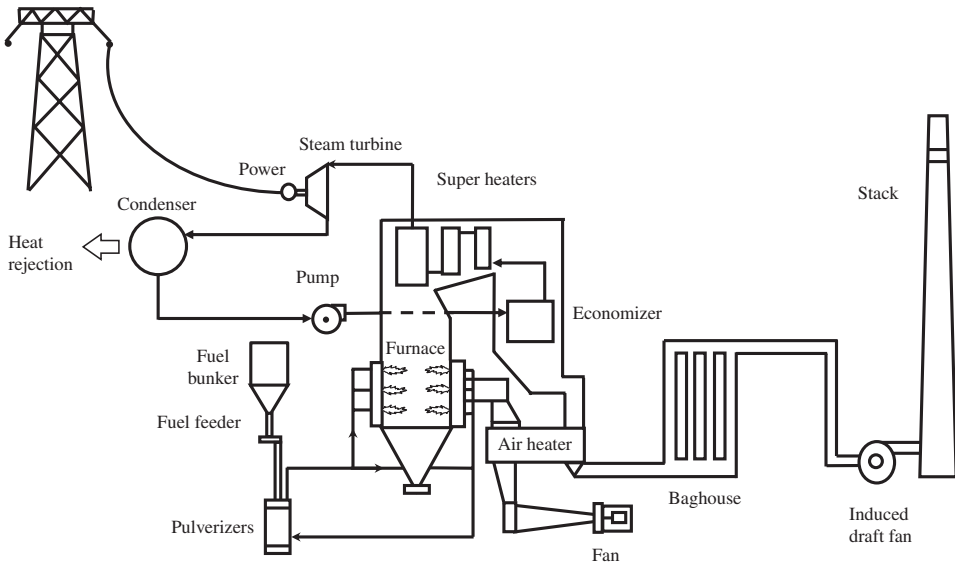


FIG. 6.2 Rankine steam power plant.

6.3.3 Rankine Cycle

The Rankine cycle is another example of an external combustion cycle. As illustrated in Figure 6.2, fuel is burned in a furnace where the released heat is transferred to pressurized water contained within steel tubes. Steam generated in this process is expanded in a steam turbine, which drives an electric generator to produce electric power. The steam is condensed in a water-cooled condenser, which controls the temperature exiting the turbine and thus sets T_L in Equation 6.1.

The Rankine steam power cycle has been the foundation of stationary power generation for over a century. Although Brayton cycles employing gas turbines and electrochemical cycles based on fuel cells will constitute much of the growth in power generation in the future, steam power plants will continue to supply the majority of electric power for decades to come and will find new applications in combination with advanced generation technologies. The reason for the Rankine cycle's preeminence has been its ability to directly fire coal and other inexpensive fuels. Constructed at scales of several hundred megawatts, the modern steam power plant can convert as much as 45% of chemical energy in fuel to electricity at a cost of \$0.02–\$0.05 per kilowatt.

Utility-scale steam power plants are not expected to dominate future growth in electric power infrastructure in the United States. These giant plants take several years to plan and construct, which decreases their financial attractiveness in increasingly deregulated power markets. Coal and other fossil fuels burned

in these plants are major sources of air pollution, including sulfur and nitrogen oxides, both of which are precursors to acid rain and the latter an important factor in smog formation; fine particulate matter, which is implicated in respiratory disease in urban areas; and heavy metals, the most prominent being mercury, which accumulates in the biosphere to toxic levels. Substitution of biorenewable resources such as wood and agricultural residues for coal in existing power plants could substantially reduce pollution emissions, although these plants are so large that the locally available biomass resources could supplant only a small fraction of the total energy requirement. Small-scale steam power plants sized for use of local biomass resources have low thermodynamic efficiencies, on the order of 25%, making them wasteful of energy resources.

6.3.4 Brayton Cycle

The Brayton cycle produces electric power by expanding hot gas through a turbine. These gas turbines operate at temperatures approaching 1300°C compared to inlet temperatures of less than 650°C for steam turbines used in Rankine cycles. Although this difference in inlet temperature (T_H in Equation 6.1) would suggest that Brayton cycles have much higher thermodynamic efficiencies than Rankine cycles, the Brayton cycle also has much higher exhaust temperature (T_L in Equation 6.1) than does the Rankine cycle. Gas turbine exhaust temperatures are in the range of 400–600°C, whereas steam turbine exhaust temperatures are on the order of 20°C. Furthermore, Brayton cycles, which contain both a gas compressor and gas turbine, have more sources of mechanical irreversibilities, further degrading thermodynamic efficiencies, which may only be marginally higher than the best Rankine steam cycles. However, improvements in gas turbine technology that allow operation at higher temperatures and pressures are expected to increase Brayton cycle efficiency for large power plants to greater than 50%, although 30% is more realistic for gas turbines sized appropriately for biomass power plants.

The two general classes of gas turbines for power generation are heavy-duty industrial turbines and lightweight aeroderivative gas turbines. The aeroderivatives are gas turbines originally developed for commercial aviation but adapted for stationary electric power generation. They are attractive for biopower applications because of their high efficiency and low unit capital costs at the modest scales required for biomass fuels.

Gas turbines are well suited to gaseous and liquid fuels, which are relatively free of contaminants that rapidly erode or corrode turbine blades. In this respect, gas turbine engines are not suitable for directly firing most biomass fuels. Solid biomass releases significant quantities of alkali metals, chlorine, mineral matter, and lesser amounts of sulfur upon burning. These would be entrained in the gas flow entering the expansion turbine where they would quickly contribute to blade failure. Cleaning large quantities of hot flue gas is not generally considered an

economical proposition. Even the gas released from anaerobic digestion contains too much hydrogen sulfide to be directly burned in a gas turbine without first chemically scrubbing the gas to remove this corrosive agent.

Nevertheless, gas turbine engines are considered one of the most promising technologies for biopower because of the relative ease of plant construction, cost-effectiveness in a wide range of sizes (from tens of kilowatts to hundreds of megawatts), and the potential for very high thermodynamic efficiencies when employed in advanced cycles. The key to their success in biopower applications is converting the biomass to clean-burning gas or liquid before burning it in the gas turbine combustor. Chapter 8 explores technologies suitable for this purpose.

6.3.5 Combined Cycles

In an effort to enhance energy conversion efficiency, combined cycle power systems have been developed, which recognize that waste heat from one power cycle can be used to drive a second power cycle. Combined cycles would be unnecessary if a single heat engine could be built to operate between the temperature extremes of burning fuel (T_H) and the ambient environment (T_L). However, temperature and pressure limitations on materials of construction have prevented this realization. Combined cycles employ a topping cycle designed to operate between T_H and some intermediate temperature T_I and a bottoming cycle designed to operate between T_I and T_L . The overall efficiency of a combined cycle power system is

$$\eta_C = \eta_T + \eta_B - \eta_T \eta_B \quad (6.2)$$

where η_C , η_T , and η_B are the efficiencies of the combined cycle, topping cycle, and bottoming cycle, respectively. Most commonly, combined cycle power plants employ a gas turbine engine for the topping cycle and a steam turbine plant for the bottoming cycle, achieving overall efficiencies of 60% or higher.

Clean-burning fuel from biomass for use in a combined cycle can be obtained by thermal gasification or anaerobic digestion to produce gas or by fast pyrolysis to produce liquid. Integrated gasification/combined cycle (IGCC) power is illustrated in Figure 6.3. Compressed air enters an oxygen plant, which separates oxygen from the air. The oxygen is used to gasify biomass in a pressurized gasifier to produce medium heating-value producer gas. The producer gas passes through cyclones and a gas clean-up system to remove particulate matter, tar, and other contaminants that may adversely affect gas turbine performance (alkali and chloride being the most prominent among these). These clean-up operations are best performed at high temperature and pressure to achieve high cycle efficiency. The clean gas is then burned in air and expanded through a gas turbine operating as a “topping” cycle. The gas exits the turbine at temperatures ranging between 400°C and 600°C. A heat recovery steam generator produces steam for a “bottoming” cycle that employs

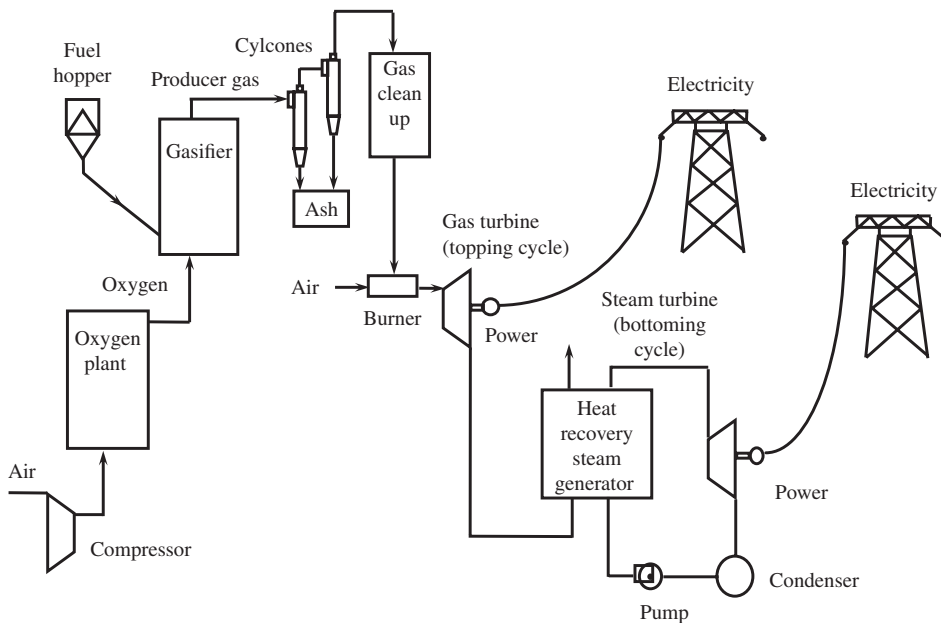


FIG. 6.3 Integrated gasification/combined cycle power plant based on a gas turbine topping cycle.

a steam turbine. Electric power is produced at two locations in this plant, yielding thermodynamic efficiencies exceeding 47%.

IGCC systems based on gas turbines are attractive for several reasons. These reasons include their relative commercial readiness and the expectation that they can generate electricity at the lowest cost of all possible biomass power options.

An alternative to IGCC is to generate steam for injection into the gas turbine combustor, which increases mass flow and power output from the turbine. This variation, called a steam-injected gas turbine (STIG) cycle, is less capital intensive than IGCC, since it does not employ a steam turbine. The STIG cycle is commercially developed for natural gas; lower flammability limits for producer gas make steam injection more problematic for biomass-derived producer gas. The intercooled steam-injected gas turbine (ISTIG) is an advanced version of the STIG. This cycle further improves thermodynamic efficiency by cooling gas flow between several stages of compression (intercooling).

6.3.6 Fuels Cells

Among the most exciting new energy technologies are fuel cells, which directly convert chemical energy into work, thus bypassing the restriction on efficiency imposed by the Carnot relationship. This does not imply that fuel cells can convert

100% of chemical enthalpy of a fuel into work, as the process still must conform to the laws of thermodynamics. Thermodynamic efficiency, as defined in Chapter 2, is the ratio of useful energy out to the total energy into the process. For a fuel cell, the useful energy out is the electrical work generated. From thermodynamics, it is known that the maximum theoretical work for a chemical reaction is equal to the change in Gibbs function ΔG for the reaction. The total chemical energy entering the fuel cell is the enthalpy of reaction ΔH . Therefore, the maximum efficiency of a fuel cell operating at 1 atm of pressure is

$$\eta_{\max} = \frac{E_{\text{out}}}{E_{\text{in}}} = \frac{\Delta G^{\circ}}{\Delta H^{\circ}} = \frac{\Delta H^{\circ} - T\Delta S^{\circ}}{\Delta H^{\circ}} = 1 - T \frac{\Delta S^{\circ}}{\Delta H^{\circ}} \quad (6.3)$$

where the superscript indicates calculation at 1 atm of pressure. All practical fuel cells to date are based on the oxidation of hydrogen:



which has an enthalpy of reaction of $-285\,830$ kJ/kmol and entropy of reaction of -163 kJ/kmol-K at 25°C . Thus, a fuel cell operating at 25°C (298 K) has a theoretical maximum efficiency of

$$\eta_{\max} = \left[1 - 298\text{K} \frac{(-163 \text{ kJ/kmol-K})}{(-285\,830 \text{ kJ/kmol})} \right] \times 100 = 83\% \quad (6.5)$$

Irreversibilities acting on the fuel cell reduce this efficiency to 35–60%, depending upon the fuel cell design. Thus, fuel cells can produce significantly more work from a given amount of fuel than can heat engines. However, carbonaceous fuels must first be reformed to hydrogen before they are suitable for use in fuel cells. The energy losses associated with fuel reforming must be included when determining the overall fuel-to-electricity conversion efficiency of a fuel cell.

The operation of a fuel cell is illustrated schematically in Figure 6.4. The device consists of two gas-permeable electrodes separated by an electrolyte, which is a transport medium for electrically charged ions. Hydrogen gas, the ultimate fuel in all current designs of fuel cells, enters the fuel cell through the anode, while oxygen is admitted through the cathode.

Depending on the fuel cell design, either positively charged hydrogen ions form at the anode or negatively charged ions containing oxygen form at the cathode. In either case, the resulting ions migrate through the electrolyte to the opposite electrode from which they are formed. Hydrogen ions migrate to the cathode where they react with oxygen to form water. Oxygen-bearing ions migrate to the anode where they react with hydrogen to form water. Both ionic processes release chemical

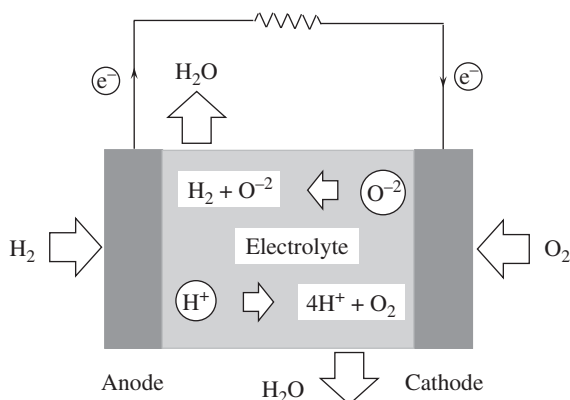


FIG. 6.4 Schematic of operation of fuel cell.

energy in the form of electrons at the anode, which flow to the cathode through an external electric circuit. This external flow of electrons represents the direct generation of electric power from flameless oxidation of fuel. The inherently high thermodynamic efficiency of fuel cells makes them attractive for biomass power where fuel costs are relatively expensive compared to many fossil fuels.

Several types of fuel cells have been developed, which are classified according to the kind of electrolyte employed: phosphoric acid, polymeric, molten carbonate, and solid oxide. Despite differences in materials and operating conditions, all are based on the electrochemical reaction of hydrogen and oxygen. For integrated gasification/fuel cell power systems, the molten carbonate and solid oxide systems are of particular interest because of their high-temperature operation, which allows waste heat recovery and use in advanced power cycles.

The first generation of fuel cells employs phosphoric acid as the electrolyte. Operated at 200°C , it attains efficiencies of 35–45%. Although well developed, commercial application has been limited by its use of expensive platinum catalysts, which are deactivated by CO.

Proton exchange membrane fuel cells were originally developed for space applications but are also considered attractive for automotive propulsion. The electrolyte is a solid polymeric material operated at less than 100°C ; both factors contribute to the ease of construction and operation of this fuel cell. Efficiencies range between 35% and 60%. However, this fuel cell is intolerant of CO, which can be difficult to exclude from on-board reformed fuels. It would also require the use of “cold” gas, which reduces the efficiency of a gasification-based power system.

The molten carbonate fuel cell operates at about 650°C . Although hydrogen is the ultimate energy carrier, this fuel cell can be operated on a variety of hydrogen-rich fuels, including methane, kerosene, diesel fuel, ethanol, and producer gas. Within the fuel cell, a reformer converts these fuels into mixtures of hydrogen,

carbon monoxide, carbon dioxide, and water along with varying amounts of unreformed fuel. Overall efficiency of converting methane into electricity is 45–55%. Molten carbonate fuel cells have completed extensive demonstration trials, but they have unresolved materials problems related to the use of corrosive alkali carbonate as electrolyte.

The solid oxide system is also a high-temperature fuel cell, operating at 650–1000°C. The electrolyte is a porous ceramic material, usually based upon yttrium and zirconium. The solid electrolyte provides for a simpler, less expensive design and longer expected life than other fuel cell systems. Efficiencies are between 50% and 60%. The higher operating temperature compared to the molten carbonate system also enhances its attractiveness for heat recovery and use in advanced power systems. Most solid oxide fuel cells operate with a steam reformer in which water vapor and carbon monoxide react according to the water–gas shift reaction to produce hydrogen, thus making them compatible with carbon monoxide-rich producer gas as fuel. Solid oxide systems may solve some of the corrosion problems associated with molten carbonate fuel cells.

The gas mixture produced by a biomass gasifier contains dust and tar that must be removed or greatly reduced for most applications, including power generation in fuel cells. Removal of tar would ideally be performed at elevated temperatures. If the gas is to be used in fuel cells, further cleaning is required to remove ammonia (NH₃), hydrogen chloride (HCl), and hydrogen sulfide (H₂S). Table 6.1 details contaminant removal requirements for various kinds of fuel cells. To obtain high energy efficiency, trace contaminant removal must be performed at elevated temperatures for fuel cells that operate at relatively high temperatures. Low-temperature fuel cells cannot tolerate CO, which can be removed by the water–gas shift reaction. The catalysts that facilitate the shift reaction, however, are poisoned by trace contaminants, which must be removed prior to the shift reactors. One method for removing H₂S and HCl is the use of a fixed bed of calcined dolomite or limestone and zinc titanate at temperatures around 630°C. This is followed by steam reforming at high temperature (750–850°C) to destroy tar and ammonia.

Table 6.1 Contaminants for various fuel cell systems

Fuel Cell Type	Classification	Contaminant Tolerance Level			
		H ₂ S	HCl	NH ₃	CO
Solid polymer	Low temperature	–	–	–	10 ppm
Phosphoric acid	Low temperature	50 ppm	–	–	5%
Molten carbonate	High temperature	0.5 ppm	10 ppm	1%	–
Solid oxide	High temperature	0.1 ppm	1.0 ppm	0.5%	–

Source: US Department of Energy National Energy Technology Laboratory (2000) *Fuel Cell Handbook*, 5th edn. CD-ROM. Morgantown, WV/Pittsburgh, PA: US Department of Energy National Energy Technology Laboratory.

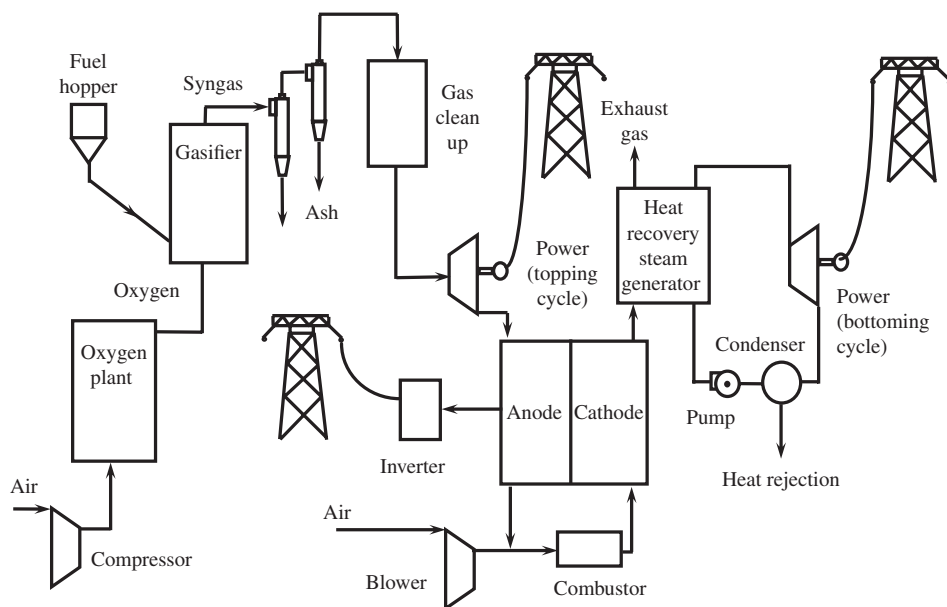


FIG. 6.5 Combined cycle power plant based on high-temperature fuel cells.

Figure 6.5 illustrates an IGCC power plant based on a molten carbonate fuel cell. Biomass is gasified in oxygen to yield producer gas. Gasification occurs at elevated pressure to improve the yield of methane, which is important for proper thermal balance of this fuel cell. Hot-gas clean up to remove particulate matter, tar, and other contaminants is followed by expansion through a gas turbine as part of a topping power cycle. The pressure and temperature of the producer gas is sufficiently reduced after this to admit it into the fuel cell. High-temperature exhaust gas exiting the cathode of the fuel cell enters a heat recovery steam generator, which is a part of a bottoming cycle in the integrated plant. Thus, electricity is generated at three locations in the plant for an overall thermodynamic efficiency reaching 60% or more.

6.4 Biofuels

Almost 25% of energy consumption in the United States is consumed by transportation needs. Approximately 40% of this amount comes from imported petroleum. Thus, development of transportation fuels from biorenewable resources is a priority if decreased dependence on foreign sources of energy is to be achieved.

Traditional transportation fuels exploit the different boiling points of hydrocarbons that make up petroleum (see Figure 6.6). Boiling point increases as the

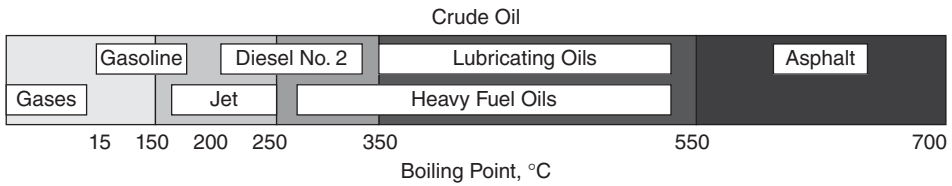


FIG. 6.6 Conventional transportation fuels exploit the wide range of boiling points of petroleum hydrocarbons (note that the high molecular weights of high-boiling-point hydrocarbons can be cracked to smaller molecules).

molecular weight of hydrocarbons increases. Large hydrocarbon molecules can be cracked to smaller molecules with lower boiling points that are suitable as fuels although this requires the additional expenditure of energy and equipment.

The hydrocarbons making up traditional transportation fuels include chains of single-bonded carbon atoms known as straight-chain alkanes or paraffins, branched-chain alkanes known as isoparaffins, rings of single-bonded carbon atoms known as cycloalkanes (sometimes referred to as naphthenes), and six-member rings of carbon with alternating single and double bonds known as aromatics. For example, as illustrated in Figure 6.7, gasoline contains C_6 molecules in one of several forms including straight-chain hexane (*n*-hexane), a branched-chain hexane (isohexane), a saturated ring (cyclohexane), or an aromatic ring (benzene). Traditional transportation fuels are classified as gasoline, diesel fuel, or jet fuel.

Gasoline is intended for spark-ignition (Otto cycle) engines; thus, it is relatively volatile but resistant to autoignition during compression. Diesel fuel is intended for use in compression-ignition (Diesel cycle) engines; thus, it is less volatile compared to gasoline and more susceptible to autoignition during compression. Jet fuel is designed for use in gas turbine (Brayton cycle) engines, which are not limited by autoignition characteristics but otherwise have very strict fuel specifications for reasons of safety and engine durability. Gasoline is a mixture of hundreds of

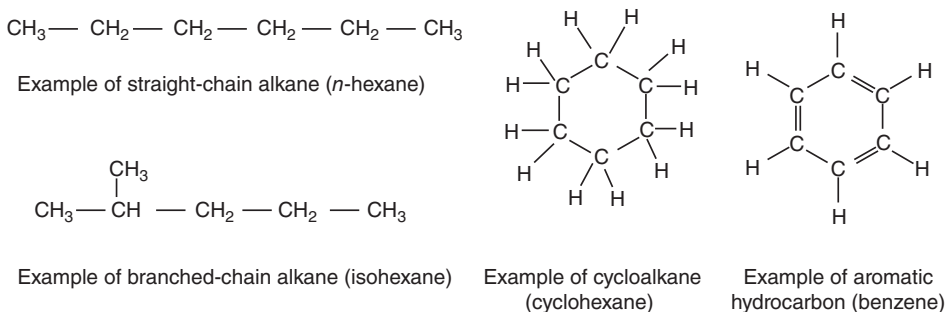


FIG. 6.7 Examples of six-carbon atom hydrocarbon molecules found in petroleum-derived transportation fuels.

different hydrocarbons obtained from a large number of refinery process streams that contain between 4 and 12 carbon atoms with boiling points in the range of 25–225°C. Most of the mixture consists of alkanes with butanes and pentanes added to meet vapor pressure specifications. A few percent of aromatic compounds are added to increase octane number, the figure of merit used to indicate the tendency of a fuel to undergo premature detonation within the combustion cylinder of an internal combustion engine. The higher the octane number, the less likely a fuel will detonate until exposed to an ignition source (electrical spark). Premature denotation is responsible for the phenomenon known as engine knock, which reduces fuel economy and can damage an engine. Various systems of octane rating have been developed, including research octane and motor octane numbers. Federal regulation in the United States requires gasoline sold commercially to be rated using an average of the research and motor octane numbers. Gasoline rated as “regular” has a commercial octane number of about 87 while premium grade is 93.

Diesel fuel, like gasoline, is also a mixture of light distillate hydrocarbons but with lower volatility and higher viscosity. Because diesel fuel is intended to be ignited by compression rather than by a spark, its autoignition temperature is lower than for gasoline. The combustion behavior of diesel fuels is conveniently rated according to cetane number, an indication of how long it takes a fuel to ignite (ignition delay) after it has been injected under pressure into a diesel engine. A high cetane number indicates short ignition delay; for example, No. 2 diesel fuel has cetane number of 37–56, while gasoline has a cetane number less than 15.

Jet fuel is designated as either kerosene type (including Jet A, Jet A1, and JP8) or wide cut type (including Jet B and JP4). Kerosene type is a mixture of straight-chain alkane (paraffin) molecules containing 9–20 carbon atoms giving it a relatively high boiling range of 165–290°C, making it similar to diesel fuel. It also contains a certain percentage of aromatic compounds to meet desired fuel performance characteristics. Wide-cut-type jet fuel is a blend of kerosene and gasoline containing 5–15 carbon atoms, which gives it a wider boiling point range. It contains straight-chain and branched-chain alkane molecules as well as aromatic hydrocarbons. Although its lower boiling point range enhances cold-weather performance, it also makes it more flammable and dangerous to handle. At one time it was preferred in the United States because of the wide availability of gasoline for blending with more scarce kerosene. However, safety and environmental concerns have resulted in the phase out of wide-cut-type blends for both commercial and military aviation except in demanding applications.

The primary candidates for liquid biofuels are methanol, ethanol, butanol, biodiesel, and biomass-derived hydrocarbons. Methanol, ethanol, and butanol, by virtue of their high octane numbers, are suitable for use in spark-ignition engines. The high cetane numbers of biodiesel, which are methyl or ethyl esters formulated from vegetable or animal fats, make them suitable for use in compression-ignition engines. Biomass-derived hydrocarbons, depending upon their composition, can

Table 6.2 Comparison of transportation fuels

	Gasoline Hydrocarbons	No. 2 Diesel Fuel Hydrocarbons	Methanol, CH ₃ OH	Ethanol, C ₂ H ₅ OH	Butanol, C ₄ H ₉ OH	Biodiesel, Methyl Ester
Specific gravity at 16°C	0.72–0.78	0.85	0.796	0.794	0.81	0.886
Kinematic viscosity at 20°C (m/s)	0.8×10^{-6}	2.5×10^{-6}	0.75×10^{-6}	1.4×10^{-6}	3.2×10^{-6}	3.9×10^{-6}
Boiling point range ^a (°C)	30–225	210–235	65	78	118	315–350
Flash point (°C)	–43	52	11	13	35	100–170
Autoignition temperature (°C)	370	254	464	423	343	–
Octane no. (research)	91–100	–	106	107	96	–
Octane no. (motor)	82–92	–	92	89	78	–
Cetane no.	<15	37–56	<15	<15	–	55
Heat of vaporization (kJ/kg)	380	375	1185	920	430	–
Lower heating value (MJ/kg)	43.5	45	20.1	27	35.4	37
Vapor pressure (psi at 100F)	4.5	–	4.6	2	0.33	–

Source: Borman, G.L. and Ragland, K.W. (1998) *Combustion Engineering*. McGraw-Hill.^aSeasonally adjusted for cold and hot weather operation.

be used as direct substitutes for gasoline, diesel, and jet fuel. Properties of these fuels are compared in Table 6.2.

6.4.1 Methanol

In the 1980s, production of methanol from coal was touted as an alternative to petroleum-based fuels. The same process of gasification and fuel synthesis can be used to produce methanol from biomass. Methanol as fuel is characterized by narrow boiling point range, high heat of vaporization, and high octane number. It has only 49% of the volumetric heating value of gasoline. As fuel, methanol has many of the same advantages and disadvantages as ethanol but has not met the same acceptance as ethanol for two reasons. First, although biomass-to-methanol is economically attractive compared to many alternative routes to biofuels, the capital investment for gasification and catalytic synthesis equipment is very high. In contrast, ethanol can be fermented from sugar or starch crops for relatively modest capital investment. Second, methanol is considerably more toxic than ethanol. The closely related and similarly toxic methyl tertiary butyl ether (MTBE) has been banned as fuel oxygenate and octane enhancer because of concerns about ground water contamination. Thus, it seems unlikely that methanol will ever be a serious contender as biofuel. On the other hand, as described in Chapter 8, methanol can be converted to gasoline, which is a more attractive route for transportation fuel from biomass.

6.4.2 Ethanol

Ethanol can be produced by the fermentation of sugar or starch crops. A fuel ethanol market has been developed in Brazil based on sugarcane, while the United States has relied on cornstarch for commercial production of fuel ethanol. Technologies are also being developed to convert lignocellulose into sugars or syngas, a mixture of carbon monoxide and hydrogen, either of which can be fermented into ethanol.

On a volumetric basis, ethanol has only 66% of the heating value of gasoline. Thus, the range of a vehicle operating on pure ethanol is theoretically reduced by a corresponding amount and, accordingly, meaningful comparisons of the cost of gasoline and ethanol should be made on the basis of energy delivered (\$/GJ) instead of fuel volume (\$/L). However, fuel economy depends on many complex interactions between a fuel and the combustion environment within an engine, which some argue improves the relative performance of ethanol. For example, as Table 6.2 illustrates, ethanol has a higher latent heat of vaporization compared to gasoline. This promotes cooler operation of the engine, allowing higher densities of fuel and air to be burned in the engine. Furthermore, ethanol, with molecular formula of C_2H_5OH , has a much lower stoichiometric air–fuel ratio than gasoline, nominally taken to have the molecular formula of octane (C_8H_{18}); thus a higher energy density can be achieved in the engine. These factors result in higher inducted fuel energy densities, which can produce both higher power outputs and improved engine efficiency compared to gasoline-fueled vehicles. Finally, the higher octane number for ethanol compared to gasoline (109 vs. 91–101) allows engines to be designed to run at higher compression ratios, which improves both power and fuel economies. Estimates for efficiency improvements in engines optimized for ethanol instead of gasoline range from 15% to 30%, resulting in a driving range approaching 80% of that of gasoline.

Internal combustion engines can be fueled on pure ethanol (known as neat alcohol or E100) or blends of ethanol and gasoline. Brazil employs 190 proof ethanol (95 vol% alcohol and 5% water), which eliminates the energy-consuming step of producing anhydrous ethanol. In the United States two ethanol–gasoline blends are common: E85 contains 85% ethanol and 15% gasoline and E10, at one time referred to as gasohol, contains only 10% ethanol with the balance being gasoline. The advantage of E10 is that it can be used in vehicles with engines designed for gasoline; however, its use is accompanied by a loss in fuel economy (as measured in km/L or miles/gal) compared to gasoline, amounting to 2–5%.

A significant problem with ethanol–gasoline blends is water-induced phase separation. Water contaminating a storage tank or pipeline is readily absorbed by ethanol, resulting in a lower water-rich layer and an upper hydrocarbon-rich layer, which interferes with proper engine operation. Water contamination is a problem that has not been fully addressed by the refining, blending, and distribution

industries; thus, transportation of ethanol–gasoline blends in pipelines is not permitted in the United States and long-term storage is to be avoided.

6.4.3 Butanol

Butanol (C_4H_9OH), by virtue of its longer carbon chain length, is less soluble in water and has higher heating value than methanol and ethanol. For this reason, butanol has some attraction as motor fuel. Its energy content is within 10% of gasoline and its octane number, although lower than ethanol, is greater than gasoline's. Its low vapor pressure is attractive in reducing volatile organic matter emissions, but it can make cold starting more difficult. Butanol is only moderately soluble in water, an important advantage compared to fully soluble methanol and ethanol. Although not currently used as transportation fuel, very likely butanol would be substituted for ethanol if its fermentation from sugar or starch crops became economically feasible.

6.4.4 Biodiesel

Vegetable oils, which are triglycerides of fatty acids, have long been recognized as potential fuels in diesel engines. Compared to petroleum-based diesel fuels, vegetable oils have higher viscosity and lower volatility, which result in fouling of engine valves and less favorable combustion performance, especially in direct-injection engines. The solution to this problem is to convert the triglycerides into methyl esters or ethyl esters of the fatty acids, known as biodiesel, and the byproduct 1,2,3-propanetriol (glycerol).

Table 6.2 illustrates that fuel properties of biodiesel are very similar to petroleum-based diesel. The specific gravity and viscosity of biodiesel are only slightly higher than for diesel, while the cetane numbers and heating values are comparable. Significantly higher flash points for biodiesel represent greater safety in storage and transportation. Biodiesel can be used in unmodified diesel engines with no excess wear or operational problems. Tests in light and heavy trucks showed few differences other than a requirement for more frequent oil changes because of the buildup of ester fuel in engine crankcases.

6.5 Chemicals

Chemicals are the broadest class of biobased products. It would be impossible to describe all possible chemical products from biorenewable resources in this section. Instead, an effort is made to focus on potential commodity chemicals from biorenewable resources although fine chemicals and pharmaceuticals are also potential products. Table 6.3 lists the top 60 commodity chemicals in the United States in terms of their annual production. The feedstock employed and

Table 6.3 Sixty major organic chemicals manufactured in the United States

No.	Product	Annual Production (10 ⁹ kg)	Usual Organic Feedstock	Energy Consumed per Product Mass		Average Market Price (\$/kg)
				Process (MJ/kg)	Feed (MJ/kg)	
1.	Ethylene	21.30	Natural gas liquids	23.3	58.1	0.55
2.	Propylene	11.65	Natural gas liquids	16.3	56.8	0.42
3.	MTBE	7.99	C ₄ H ₈ /methanol	13.0	50.5	0.29
4.	Ethylene dichloride	7.83	C ₂ H ₄	4.0	42.2	0.37
5.	Benzene	7.24	BTX	2.3	81.2	0.33
6.	Urea	7.07	CO ₂ (NH ₃)	2.8	30.6	0.20
7.	Vinyl chloride	6.79	C ₂ H ₄	17.4	53.4	0.45
8.	Ethylbenzene	6.19	C ₂ H ₄ /benzene	2.3	66.5	0.56
9.	Styrene	5.16	Ethylbenzene	12.8	74.3	0.64
10.	Methanol, synthetic	5.12	CO/(H ₂)	11.6	25.8	0.21
11.	Mixed xylenes	4.25	BTX	10.2	43.0	0.31
12.	Ethanol, fermentation	3.90	Corn	18.8	31.0	0.42
13.	Formaldehyde (37 wt%)	3.68	Methanol	0.0	43.9	0.24
14.	Terephthalic acid	3.61	<i>p</i> -Xylene	12.8	57.8	0.88
15.	Ethylene oxide	3.46	C ₂ H ₄	0.4	68.1	0.99
16.	Toluene	3.05	BTX	10.2	43.0	0.31
17.	<i>p</i> -Xylene	2.88	BTX	22.3	59.1	0.46
18.	Cumene	2.55	C ₃ H ₆ /benzene	2.3	66.2	0.51
19.	Ethylene glycol	2.37	Ethylene oxide	13.9	49.6	0.37
20.	Acetic acid, synthetic	2.12	Methanol/(CO)	10.7	27.7	0.79
21.	Phenol, synthetic	1.89	Cumene	15.1	99.3	0.90
22.	Propylene oxide	1.81	Propylene	16.3	58.4	1.41
23.	1,3-Butadiene	1.67	Butanes/enes	51.1	58.4	0.49
24.	Carbon black	1.51	Residual oil	27.9	93.0	0.64
25.	Isobutylene	1.47	Butanes/enes	9.3	85.3	0.68
26.	Acrylonitrile	1.45	Propylene	6.0	78.8	1.17
27.	Vinyl acetate	1.31	C ₂ H ₄ /HOAc	15.6	59.2	0.97
28.	Acetone	1.25	Cumene	15.1	99.3	0.86
29.	Butraldehyde	1.22	Propylene/(CO)			0.95
30.	Cyclohexane	0.969	Benzene	2.3	58.1	0.44
31.	Adipic acid	0.816	Cyclohexane	29.1	84.0	1.62
32.	Nitrobenzene	0.748	Benzene			0.73
33.	Bisphenol A	0.736	Acetone/phenol			2.07
34.	Caprolactam	0.714	Cyclohexanone	7.9	54.5	2.05
35.	Acrylic acid	0.698	Propylene			1.92
34.	Caprolactam	0.714	Cyclohexanone	7.9	54.5	2.05
35.	Acrylic acid	0.698	Propylene			1.92
36.	<i>n</i> -Butanol	0.677	Propylene (CO)			1.10
37.	Isopropyl alcohol	0.646	Propylene			0.71
38.	Aniline	0.631	Nitrobenzene			1.08
39.	Methyl methacrylate	0.622	Acetone/(HCN)			1.32
40.	Cyclohexanone	0.501	Phenol			1.61
41.	Methyl chloride	0.483	Methane			0.85
42.	<i>o</i> -Xylene	0.465	BTX			0.42
43.	Propylene glycol	0.462	Propylene oxide			1.43
44.	Phthalic anhydride	0.451	Naphthalene			0.84
45.	Acetone cyanohydrin	0.410	Acetone/(HCN)			0.77
46.	Toluene diisocyanates	0.395	Toluene			2.09

(continued)

Table 6.3 (Continued)

No.	Product	Annual Production (10 ⁹ kg)	Usual Organic Feedstock	Energy Consumed per Product Mass		Average Market Price (\$/kg)
				Process (MJ/kg)	Feed (MJ/kg)	
47.	Dodecylbenzene	0.386	C ₆ H ₆ /dodecene			1.25
48.	Ethanol amines	0.369	Ethylene oxide			1.26
49.	Diethylene glycol	0.354	Ethylene oxide			0.71
50.	Carbon tetrachloride	0.344	Methane			0.79
51.	2-Ethyl-1-hexanol	0.337	C ₃ H ₆ /CO or RCHO			1.23
52.	Ethanol, synthetic	0.284	Ethylene	4.7	31.4	0.42
53.	Isoprene	0.281	HC/turpentines			0.68
54.	1,4-Butanediol	0.266	C ₃ H ₆ /CO or THF			1.24
55.	Methyl ethyl ketone	0.264	2-Butanol			1.01
56.	Ligninsulfonic acid salt	0.258	Sulfite liquor			0.36
57.	Chloroform	0.256	Methane			0.87
58.	Maleic anhydride	0.251	Benzene			0.93
59.	C12-benzenesulfonate Na	0.217	C ₆ H ₆ /dodecene			1.34
60.	1-Butene	0.209	Ethylene			0.57

Source: Klass, D.L. (1998) *Biomass for Renewable Energy, Fuels, and Chemicals*. San Diego: Academic Press.

the energy consumed in their production as well as their selling prices in 1995 are also listed (prices of commodity chemicals can fluctuate widely, even during the course of a year, so current market reports should be consulted if accurate prices are important).

In principle, all organic compounds can be synthesized from biorenewable resources. In practice, current economics favors chemical synthesis from fossil resources, especially from petroleum and natural gas, except for a few oxygenated organic compounds. The following three sections summarize three categories of potential biobased chemicals: commercially important chemicals that are currently produced from fossil resources but could also be produced from biorenewable resources, those that are currently produced from biorenewable resources, and unexploited chemicals with future potential in the manufacture of biobased products.

6.5.1 Chemicals Produced from Fossil Resources

The petrochemical industry is built on seven basic building blocks: syngas from methane (CH₄), ethylene (ethene—C₂H₄), propylene (propene—C₃H₆), butanes (C₄H₁₀), butylene (butene—C₄H₈), butadiene (C₄H₆), and BTX, the latter of which is a mixture of the closely related compounds benzene, toluene (methylbenzene), and xylene (dimethylbenzene). Methane is obtained from natural gas. Ethylene, propylene, butane, butylene, and butadiene are obtained from natural gas liquids, refinery off-gases, and petroleum. Benzene, toluene, and xylene, the basis for aromatic compounds, are obtained from petroleum and coal. From these

seven building blocks, all the organic compounds of the modern world can be obtained.

The following paragraphs describe several industrially important organic compounds, currently obtained from fossil resources that might be obtained in the future from biorenewable resources.

Ethylene

Ethylene is the leading organic chemical manufactured in the United States and is the starting point for a wide variety of consumer and industrial products including polymers (polyethylene, polystyrene, and polyester) and polyols (ethylene glycol). It is commercially produced from natural gas liquids.

Ethylene can also be produced by dehydration of ethanol in the presence of an acid catalyst. Thus, some have suggested the conversion of inexpensive lignocellulosic biomass into ethanol followed by the manufacture of biobased ethylene. Although Brazil built a commodity chemical industry on this process, the relatively low cost of natural gas makes this an unlikely prospect in other markets for the foreseeable future.

1,3-Butadiene

Sixty percent of 1,3-butadiene (C_4H_6) production in the United States is used to produce elastomers such as styrene/butadiene, polybutadiene, neoprene, and nitrile rubber. The largest single market for butadiene is the manufacture of tires. Smaller amounts go into other consumer and industrial products. Butadiene is manufactured in the petroleum industry by thermal cracking of natural gas liquids.

Pentane/Pentene

Pentane (C_5H_{12}) is used as a solvent, as a blending component of high-octane gasoline, and in processing isoprene. Pentene (C_5H_{10}) is used in the formulation of plasticizers and detergents and is a precursor to the production of thiols, amines, and ammonium salts. Pentenes have been used as monomers for the manufacture of resins and low-molecular-weight thermoplastic materials. Thermal cracking of naphtha and gas oil yields ethylene and propylene as the primary products and five carbon hydrocarbons as byproducts, from which are distilled pentane and pentene.

Benzene

The single largest use of benzene (C_6H_6) in the United States is the production of styrene, which finds application in the production of such polymers as polystyrene, acrylonitrile/butadiene/styrene (ABS), styrene/acrylonitrile resins, and styrene/butadiene latexes. Benzene is also used in the manufacture of cumene (isopropyl benzene), from which comes 96% of domestic phenol production, and cyclohexane, important in the manufacture of nylon. Small amounts find uses

in the manufacture of detergents, insecticides, antioxidants, adhesives, and pharmaceuticals. Benzene is extracted from the BTX fraction obtained from catalytic reforming of naphtha.

Toluene

More than 90% of toluene (methylbenzene) is directed to the production of gasoline. Of the remaining amount, over half goes to the production of benzene, while smaller amounts are used as solvent in the production of paints and coatings and other miscellaneous products. Toluene is extracted from the BTX fraction obtained from catalytic reforming of naphtha.

Xylenes

Mixed xylenes (dimethylbenzene) consist of ortho-, meta-, and para-isomers. Separation of these isomers provides starting material for phthalic anhydride, used in plasticizers, isophthalic acid, a component of polyester resins, and dimethyl terephthalate and terephthalic acid, intermediates in the production of polyterephthalates. Mixed xylenes are also employed as solvents and in the formulation of adhesives and rubber. Xylenes are extracted from the BTX fraction obtained from catalytic reforming of naphtha.

Acetic Acid

Over 60% of acetic acid (ethanoic acid) production is used in the manufacture of vinyl acetate, the basis of white glue, laminating wallboard, and latex paint. Polymers derived from vinyl acetate find applications in the manufacture of safety glass, film products, and hot melt adhesives. About 15% is consumed in the production of acetic anhydride, most of which is converted to cellulose acetate, which is used to manufacture textile fibers, plastics, and films. About 10% of acetic acid demand supports the production of ester solvents used in the manufacture of inks, paints, and coatings. Another 10% is used to produce terephthalic acid (1,4-benzene dicarboxylic acid) and dimethyl terephthalate (dimethyl 1,4-benzene dicarboxylate) for the manufacture of fibers, resins, paints, coatings, and plastics. The production of acetic acid from fossil fuels begins with reforming of natural gas or gasification of coal to syngas. As described in Chapter 8, syngas is catalytically converted to methanol followed by catalytic carbonylation (i.e., synthesis of a carbonyl compound by the addition of carbon monoxide) to acetic acid.

Acetic acid is a metabolite from the fermentation of a variety of sugars by several organisms, including *Acetobacter aceti*, *Clostridium thermoaceticum*, and *Pachysolen tannophilus*. Acetic acid is also a major product from pyrolysis of lignocellulosic biomass. However, acetic acid from biorenewable resources is not presently cost-effective compared to production from fossil fuels.

Formic Acid

Demand for formic acid (methanoic acid) is evenly distributed in the manufacture of rubber chemicals, aluminum and nickel catalysts, leather and tanning, textiles, and other miscellaneous industries. Partial oxidation of butane, obtained from natural gas liquids, yields a mixture of carboxylic acids from which formic acid is separated.

Formic acid and three other carboxylic acids (acetic, glyceric, and lactic) can be produced by mild alkaline oxidation of dilute aqueous solutions of xylose, representing a possible path for production of biobased products. Carboxylic acids are highly water soluble, which impedes the recovery and commercial exploitation of this process.

Propionic Acid

Up to 30% of propionic acid (propanoic acid) is used to preserve grain. Another 25% is converted to sodium and calcium salts of the acid, which are used as food and feed preservatives. Production of carboxylic acid herbicides consumes another 15% with the balance used for cellulose plastics, pharmaceuticals, and solvents. Propionic acid is obtained by carbonylation of ethylene, which is derived from the pyrolysis of ethane, a constituent of natural gas.

Propionic acid is a metabolite from the fermentation of various sugars by various microorganisms including *Clostridium* species and *Propionibacterium shermanii*. The commercial production of propionic acid by fermentation is not economically viable at present.

Acrylic Acid

Acrylic acid (2-propenoic acid) is an unsaturated liquid acid that is widely used to produce acrylic esters, which are useful in the production of latexes, textiles, adhesives, sealants, and inks. Acrylic esters, which command 72% of production in acrylic acid, have increasing application as cross-linking agents for producing hard, cured surfaces. Non-ester polymers of acrylic acid have applications as flocculants, dispersants, and thickeners. New types of polyacrylic acids have recently been developed as superabsorbents such as are used in disposable diapers. A two-stage oxidation process is used to produce acrylic acid from propylene.

Succinic Acid

Succinic acid (butanedioic acid) is a crystalline dicarboxylic acid found as a common metabolite in many plants, animals, and microorganism. It is a specialty chemical with applications in food and pharmaceutical products, surfactants and detergents, biodegradable solvents and plastics, and ingredients to stimulate animal and plant growth. Its production from fossil resources begins by oxidizing butane to maleic anhydride (2,5-furandione), which is followed by reduction to succinic

anhydride (dihydro-2,5-furandione) and ring opening hydrolysis to give succinic acid.

Although a biodegradable product, for it to qualify as a biobased product, it must be produced from biorenewable resources. Efforts are under way to develop a commercial process for fermenting it from cornstarch.

Butanol

Butanol is a four-carbon alcohol (C_4H_9OH) of either of two isomeric forms (1-butanol or 2-butanol) derived from normal butane. Butanol has been suggested as an oxygenated fuel for blending with gasoline, with distinct advantages over methanol and ethanol. The energy content of butanol is closer to that of gasoline and it has no compatibility or miscibility problems with gasoline. Butanol is water tolerant; thus, it can be transported in gasoline blends by pipeline without danger of phase separation due to moisture absorption. Butanol is also a feedstock for production of butyl butyrate, often touted as a green solvent. Butanol is obtained from butane, which is extracted from natural gas liquids. Various species of *Clostridium* can ferment butanol from sugars. Like many other fermentation processes, recovery of the metabolite is a key challenge to the economics of biobased butanol.

Phenol

About 35% of phenol production goes into phenolic resins, which are primarily employed as adhesives for plywood, laminates, and insulation. About 10% of these resins are used in molding compounds for heat-resistant materials. Another 35% of phenol production supports the manufacture of polycarbonate resins, a common material in the construction of automobiles, appliances, and milk bottles, and epoxy resins, a surface coating for electronic circuit boards and a component of advanced composites. Smaller amounts of phenol are employed to manufacture nylon carpet and aniline, a useful chemical in the manufacture of inks, dyes, herbicides, and other products. Phenol is used in the production of salicylic acid, the active component of aspirin and flavorings. Phenol from petrochemicals is derived by oxidizing cumene (isopropyl benzene), which is synthesized from benzene and propylene.

6.5.2 Chemicals Produced from Biorenewable Resources

Several oxygenated organic compounds are commercially produced from biorenewable resources. In large part, these biobased products can compete in the market because synthesis routes from fossil resources to yield a comparable product have not emerged. These exceptions include lactic acid and furfural. Also commercially competitive are some cellulose derivatives, for which consumers value the intrinsic properties of the resulting biobased synthetic fibers.

Furfural and Other Furans

Furfural (2-furaldehyde) is a commercially important solvent used in the manufacture of pesticides, synthetic resins, and nylon. It is also used to produce furfuryl alcohol, which in turn is used to produce “furan resins,” important in the metal casting industry to form cores and molds. Smaller quantities of these resins are used to produce corrosion resistant grouts, mortars, joints, and valves. Some furfural is converted to tetrahydrofuran, a solvent in the resins and plastics industry.

Furfural is produced by a series of acidic dehydrations of pentoses obtained from hemicellulose-rich agricultural materials such as corncobs, oat hulls, and peanut shells. Although classified as secondary processing of biorenewable resources, in practice the dehydration of pentose occurs simultaneously with the hydrolysis of hemicellulose in a single reactor known as a digester. Sulfuric acid and biomass are blended and reacted with steam in the digester. Furfural, which boils at 160°C, appears as vapor, which exits with steam leaving the reactor. Distillation yields furfural and a wastewater stream containing about 1% acetic acid.

Furfural, illustrated in Figure 6.8a, is a member of the furan compounds, the heterocyclic aromatic series characterized by a ring structure composed of one oxygen atom and four carbon atoms. The reactivity of the furan ring allows a wide range of synthesis options. Furfural is converted to furan (Figure 6.8b), the simplest member of this series, by catalytic decarbonylation, or to furfuryl alcohol (Figure 6.8c) by hydrogenation of the aldehyde group. Furan can be converted to tetrahydrofuran (Figure 6.8d) by catalytic hydrogenation. Furfuryl alcohol can be hydrogenated to tetrahydrofurfuryl alcohol (Figure 6.8e). From tetrahydrofuran and tetrahydrofurfuryl alcohol, a wide variety of derivatives can be obtained. The ring cleavage chemistry of furan suggests the basis for synthesis of a variety of other chemicals, as well, including *n*-butanol, 1,3-butadiene, styrene, adipic acid, maleic anhydride, 1,4-butanediol, and γ -butyrolactone. Both furan and furfural have been converted to maleic anhydride.

Lactic Acid

Lactic acid (2-hydroxypropanoic acid) is a common metabolite in animals, plants, and bacteria. It is widely used in the food industry as a preservative and flavoring. Esterification with ethanol produces ethyl lactate, a solvent that also serves as a chemical intermediate. Lactate can be converted to polylactic acid (PLA) resin used

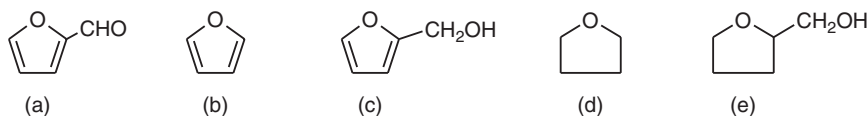


FIG. 6.8 Furan compounds synthesized from pentose: (a) furfural; (b) furan; (c) furfuryl alcohol; (d) tetrahydrofuran; (e) tetrahydrofurfuryl alcohol.

in the production of biodegradable plastic that has properties that are competitive with plastics made from polyethylene and polystyrene. Although manufacturing processes have been developed for producing lactic acid from either fossil resources or biorenewable resources, economics are increasingly favoring the use of biorenewable resources. In this case, lactic acid is produced by fermentation of glucose.

Gluconic Acid

Gluconic acid (2,3,4,5,6-pentahydroxyhexanoic acid) is converted to the chelating agent sodium gluconate, useful in removing metal ions, especially calcium, magnesium, iron, and aluminum. As such, it finds application in metal cleaning as well as equipment cleaning in the dairy and food service industries. It also has miscellaneous applications in textile, pharmaceutical, and health food industries. Gluconic acid is produced in almost quantitative yields by the oxidation of glucose in air or oxygen.

Xylitol

The pentahydric alcohol known as xylitol ($C_5H_{12}O_5$), like sorbitol and mannitol, is used as a sweetener and humidity control agent, although it has a relatively small market. It is produced from the hemicellulose fraction of birch wood. Acid hydrolysis of the finely milled wood yields the five-carbon sugar xylose and oligomers, which is removed by a hot water wash. Hydrolysis of this stream yields additional xylose, which is separated from other pentoses. Combination of xylose with hydrogen in the presence of a nickel catalyst hydrogenates the aldehyde group of xylose to yield xylitol at very high yields. Processes have also been patented for extracting the necessary xylose from corncobs and bagasse. Fermentative routes to xylitol production have also been developed. One strain of yeast, *Aureobasidium*, hydrolyzes corn fiber to xylose, while another strain, *Pichia guilliermondii*, ferments the xylose into xylitol.

Sorbitol

Sorbitol is a faintly sweet alcohol ($C_6H_{14}O_6$) derived from the catalytic hydrogenation of sucrose. Its use in toothpaste, cosmetics, and toiletries represents 32% of total domestic consumption of sorbitol. Its hygroscopic properties are employed as emollient in creams and lotions, while its cooling, sweet taste makes it suitable for mouthwashes. Sorbitol is classified as a semi-natural, nutritive sweetener with 60% of the sweetness of sucrose; thus, it is used as a confection in foods and snacks, especially mints and gums. It has applications as a bulking agent, peeling aid, and flavoring agent in the food industry. About 17% of sorbitol production is employed in the manufacture of vitamin C. Esterification of sorbitol results in a surfactant useful as a lubricant, softener, plasticizer, and anti-static agent. Sorbitol is made in very high yield by catalytic hydrogenation of isoglucose, which is produced by molybdate-catalyzed isomerization of starch-derived glucose.

Mannitol

Mannitol ($C_6H_{14}O_6$), an isomer of sorbitol, is also a slightly sweet alcohol. It finds similar applications as sorbitol, although it has a smaller market. Mannitol is a coproduct of the production of sorbitol, representing about 30% of the yield from isoglucose.

Cellulose Derivatives

Cellulose can be manipulated to produce a variety of products. Most prominent is synthetic fibers of rayon, derived from regenerated cellulose. Rayon has found application in top-weight apparel, home furnishings, and non-woven materials. Cellulose acetate fibers, another product derived from cellulose, has wide application in the textile market for soft, dyeable apparel. Cellulose ester was the first thermoplastic, widely used to manufacture tools, toys, and automobile parts; however, this market has declined in the face of competition from petroleum-derived plastics. Similarly, the cellulose ether known familiarly as cellophane was widely used by the packing industry until less costly petroleum-based products were developed. Because cellophane is biodegradable, its prospects might improve in the future. Most of these cellulose derivatives come from wood pulp.

6.5.3 Chemicals with Potential for Production from Biorenewable Resources

Levulinic Acid

Levulinic acid (4-oxopentanoic acid) has not been commercially exploited, but it may prove useful in the production of antifreeze, fuel additives, plasticizers, synthetic resins, and hydraulic brake fluids. Hydrogenation of levulinic acid yields valeric g-lactone, an excellent solvent. Levulinic acid is produced by high-temperature acid hydrolysis of hexoses (with the coproduction of formic acid) or acid treatment of tetrahydrofurfuryl alcohol.

Levogluconan

Levogluconan is an anhydrosugar derived from cellulose or starch. It is a chiral compound with potential as a building block for the production of pharmaceuticals, insecticides, new polymers, and sugar alcohols. It is currently an expensive specialty chemical, but process improvements under development could drastically reduce its cost and open the way for commercial applications. Levogluconan is produced by the fast pyrolysis of acid-treated lignocellulose with yields in the range of 20–30%. Separation techniques to yield a high purity product still need to be developed.

Hydroxyacetaldehyde

Hydroxyacetaldehyde is a carbonyl compound not currently produced commercially. However, it is a potential replacement to another carbonyl compound,

glyoxal (1,2-ethanedione), which is an important cross-linking agent in the manufacture of resins, currently produced from fossil resources. Hydroxyacetaldehyde is a coproduct in the pyrolysis of lignocellulose, with yields of about 10%.

Starch Plastics

The earliest commercial “starch plastics” were starch-filled polyethylene, a composite derived from both fossil and biorenewable resources. Although they were “bio-disintegratable,” with the starch breaking down to leave a recalcitrant polyethylene residue, they were not biodegradable in the sense of completely breaking down in relatively short time frames of a few weeks or months.

More advanced starch plastics chemically modify starch to produce polymeric material that completely degrades. For example, modification of hydroxyl groups during starch esterification yields starch esters that are thermoplastic and water resistance. Starch ester resin reinforced with natural fibers has properties comparable to general-purpose polystyrene. Formulated with plasticizers and other additives, starch ester yields resins suitable for injection-molded products.

Acetylated Wood

Acetylated wood undergoes a chemical treatment that improves dimensional stability (i.e., reduced swelling and shrinkage with moisture content) and resistance to biological degradation. The chemical treatment is a process of esterification, which can be accomplished in several different ways. Most commonly, acetic anhydride (ethanoic anhydride) is used to prepare acetylated wood, which produces acetic acid as a byproduct and unreacted acetic anhydride, which can be recycled to the acetylation reactor.

Polyhydroxybutyrate/Polyhydroxyvalerate

Polyhydroxybutyrate (PHB) and its copolymers with polyhydroxyvalerate (PHV) are melt-processable, semi-crystalline thermoplastics polyesters that are stable under everyday conditions but degrade slowly in the body and when composted or landfilled. The PHB homopolymer is stiff and rather brittle with mechanical properties resembling those of polystyrene, although it is less brittle and more temperature resistant. Copolymers are preferred for general purposes, while the homopolymer is expected to have applications in the medical and biological fields. These polymers can be prepared microbiologically from glucose or syngas. Their production in transgenic plants has also been demonstrated.

6.5.4 Synthetic Biopolymers

Polymers are used in the manufacture of a wide variety of products. Most are derived from petroleum rather than biorenewable resources. This is not because polymers are rare in nature. In fact, biologically derived polymers (biopolymers) are

Table 6.4 Common petroleum-derived polymers

Name	Formula	Applications	Market Share ^a
Polyethylene	$\left[\text{CH}_2 - \text{CH}_2 \right]_n$	LDPE—food packing, grocery bags, trash bags, squeeze bottles, industrial sheeting HDPE—milk jugs, laundry detergent bottles, containers, sporting goods, pipes, insulation, toys	36%
Poly(vinyl chloride)	$\left[\text{CH}_2 - \underset{\text{Cl}}{\text{CH}} \right]_n$	Flexible PVC—clear film and foam for packaging, floor and wall coverings, garden hose, electrical insulations, “vinyl” Rigid PVC—credit cards, pipes, building materials and components	20%
Polypropylene	$\left[\text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} \right]_n$	Packaging film, food containers, bindings, bottles, beverage crates; coatings, luggage, laboratory ware, molded automobile parts, appliances	19%
Polystyrene	$\left[\text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right]_n$	Packaging for meat, pastry, candy; expanded polystyrene (Styrofoam) used for food containers; furniture, toys, disposable dishes and utensils	9%
Poly(ethylene terephthalate)	$\left[\text{C}(=\text{O}) - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{O} \right]_n$	Beverage bottles, audio and video tape	6%

Source: Stevens, E.S. (2002) *Green Plastics: An Introduction to the New Science of Biodegradable Plastics*. Princeton, NJ: Princeton University Press.^aIncludes both thermoplastics and thermosets.

ubiquitous in nature and include polysaccharides, lignin, proteins, and polyesters. These were widely exploited in the production of manufactured product until the rise of petrochemistry, which provided inexpensive chemical building blocks from petroleum for the synthesis of versatile synthetic polymers, including polyethylene, polyvinyl chloride, polypropylene, and polystyrene (see Table 6.4). Biopolymers in the form of natural fibers continue to have many important commercial products including paper, textiles, and construction materials, as described in the next section, but they do not have the versatility of application of many synthetic polymers.

It is possible to make synthetic polymers from biorenewable resources. These synthetic biopolymers fall into two categories. The first are chemically and functionally indistinguishable from the petroleum-derived polymers listed in Table 6.4. They are produced by first converting the biorenewable resources into the same building blocks used for constructing the petroleum-derived polymers: ethylene, vinyl, propylene, and styrene, for example. From there, the synthesis route is

Table 6.5 Synthetic biopolymers

Name	Formula	Applications
Poly-3-hydroxybutyrate	$\left[\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}} \right]_n$	Biocompatible and biodegradable polyester (PHB): copolymer with PHV can yield properties resembling polyethylene or polypropylene. Products include bottles, disposable razors, eating utensils, credit cards, controlled drug release, surgical sutures
Poly-3-hydroxyvalerate	$\left[\text{O}-\underset{\text{CH}_2}{\underset{\text{CH}_3}{\text{CH}}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}} \right]_n$	Biocompatible and biodegradable polyester (PHV): copolymer with PHB can yield properties resembling polyethylene or polypropylene. Products include bottles, disposable razors, eating utensils, credit cards, controlled drug release, surgical sutures
Poly-4-hydroxybutyrate	$\left[\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}} \right]_n$	Biocompatible and biodegradable polyester: copolymer with PHV can yield properties resembling polyethylene or polypropylene. Products include bottles, disposable razors, eating utensils, credit cards, controlled drug release, surgical sutures
Poly(lactic acid)	$\left[\text{O}-\underset{\text{CH}_3}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}} \right]_n$	Water insoluble polyester: flocculating agent; synthetic fibers for textiles, compost bags, disposable eating utensils, sport equipment, paper coatings, film wrap, drug delivery systems, orthopedic materials

Source: Stevens, E.S. (2002) *Green Plastics: An Introduction to the New Science of Biodegradable Plastics*. Princeton, NJ: Princeton University Press.

identical to that of the petroleum-derived polymers. The second category consists of synthetic polymers produced from biorenewable resources that are chemically distinct from petroleum-derived polymers but share similar functionality in applications. As shown in Table 6.5, these include poly-3-hydroxybutyrate, poly-3-hydroxyvalerate, poly-4-hydroxybutyrate, and polylactic acid.

6.6 Natural Fibers

Plant fibers can be used in the manufacture of textiles, paper products, and composite materials. Cotton fibers are widely employed in the manufacture of textiles, while hardwood fibers dominate the markets for paper products and composite

Table 6.6 Comparison of properties of plant fibers to synthetic fibers

	Specific Gravity	Specific Tensile Strength (GPa)	Cost (\$/ton)
Plant fibers	0.6–1.2	1.60–2.95	200–1000
Glass	2.6	1.35	1500–2000
Kevlar	1.4	2.71	4000–6000
Carbon	1.8	1.71	8000

Source: Bolton, A.J. (1994) Natural fibres for plastic reinforcement. *Materials Technology*, 9, 12–20.

materials. Historically, herbaceous plants such as bamboo, hemp, jute, kenaf, and sisal, and crop residues, such as wheat straw and cornstover, have been sources of non-woody fiber for the production of paper and composite materials, especially during times of wood scarcity. However, the relatively higher cost of collecting and storing non-woody plant fibers and their slightly inferior properties have favored the use of wood fibers.

Non-woody plant fiber accounts for a small fraction of worldwide pulping capacity, with wheat straw accounting for more than 40% of this capacity. Much of this capacity exists in emerging markets: China, India, Pakistan, and Mexico, among others. The combination of increasing standard of living and growing shortage of wood in these countries is expected to further boost the prospects of non-woody fiber in the pulp and paper industry.

A composite is a material consisting of fibers reinforced by an adhesive matrix. In general, composites contain a large volume fraction of adhesive to avoid the occurrence of voids, which markedly degrades the strength of composite materials. Because plant fiber composites have been targeted at large volume markets, they rarely contain more than 3–12% adhesive to reduce the cost of the final product. This can be done because the polysaccharide and phenolic polymers from which plant fibers are constructed are very reactive, which makes them readily bond to adhesives compared to synthetic fibers. The inevitable presence of voids means that these products will be relegated to relatively low value applications unless developers are able to capitalize on unique properties imparted by the use of plant fibers in the composites.

As shown in Table 6.6, plant fibers can be competitive in terms of weight, specific tensile strength, and cost. Plant fibers also provide environmental advantages: less energy is consumed in producing these fibers and the resulting composites can be burned for energy at the end of the life of the product.

One of the most important features of fibers is their aspect ratio, that is, the ratio of fiber length to diameter. Plant fibers have two distinct aspect ratios: one for individual fibers and another for fiber bundles that occur naturally in plant materials, which can be extracted intact from certain non-wood plants, such as sisal, hemp, and flax. Most individual fibers have aspect ratios in the range of 100–200 with a few notable exceptions: hemp at 550, flax at 1500, cotton at 2000,

and ramie at 4000. The aspect ratio of fiber bundles varies from about 100 to over 4000, depending on the success of extracting the bundles from plant tissue. Short plant fibers are attractive as reinforcement in molding compounds and injection moldings, while longer fibers find application where anisotropy is an important property of the composites.

Two other properties of fibers will be mentioned that favor plant fibers in certain applications. Long fibers or fiber bundles can be aligned in a process known as carding in the textile industry. This ability to control fiber orientation allows anisotropic properties of strength and stiffness to be exploited. The other property, characteristic of long plant fibers, is known as drape: the ability of fabrics to flow over and follow complex shapes. This property is important in the molding of composites into complex shapes.

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