3 Other Feedstocks—Coal, Oil Shale, and Biomass

3.1 INTRODUCTION

Since the oil crises of the 1970s, the idea of deriving essential chemical feedstocks from renewable resources (renewable feedstocks) in a sustainable manner has been frequently suggested as an alternative to producing chemicals from petroleum-based feedstocks imported, under agreement, from unstable political regions with the accompanying geopolitics that go with such agreements. In addition to the geopolitics, the common petrochemical feedstocks that are derived from natural gas and crude oil are, in spite of discoveries of natural gas and crude oil, in tight formations (Chapter 2) and are depleting, such as petroleum and natural gas. The petrochemical industry uses petroleum and natural gas as feedstocks to make intermediates, which are later converted to final products that people use, such as plastics, paints, pharmaceuticals, and many others.

In spite of the apparent plentiful supply of oil in tight formation (such as the Bakken formation and the Eagle Ford formation in the United States), which may be limited in terms of total producible reserves (Wachtmeister et al., 2017) the oil industry is planning for the future since some of the most prolific basins have begun to experience reduced production rates and are reaching or already into maturity. At the same time, the demand for oil continues to grow every year, because of increased demands by the rapidly growing economies of China and India. This decline in the availability of conventional crude oil combined with this rise in demand for oil and oil-based products has put more pressure on the search for alternate energy sources (Speight, 2008, 2011a, 2011b, 2011c).

Several authors have correctly stated that petroleum is and will continue to be a major motivating force to the industrial society. Natural gas and natural gas liquids are important and their role will continue in the near future in the industrial economy. Some estimates suggest that relatively cheap hydrocarbon-based feedstocks will be available well into the next century, although predicting the availability of such feedstock beyond the next 50 years is risky (Speight, 2011a, 2011b; Speight and Islam, 2016). In fact, the reality is that the supply of crude oil, the basic feedstock for refineries and for the petrochemicals industry, is finite and its dominant position will become unsustainable as supply/demand issues erode its economic advantage over other alternative feedstocks. This situation will be mitigated to some extent by the exploitation of more technically challenging fossil resources and the introduction of new technologies for fuels and chemicals production from natural gas and coal (Speight, 2008, 2014)

More specifically, as crude oil prices continue to fluctuate (typically in an upward direction), C-1 chemistry, based on coal gasification and converting coal-derived synthesis gas to chemicals and other alternatives (such as biomass-derived chemical and biomass-derived synthesis gas) will become important. In fact, over the past two decades a series of technological advances has occurred that promise, in concert, to significantly improve the economic competitiveness of bio-based processes (Speight, 2008). Evaluation of this window of opportunity focuses on the inherent attributes of biological processes, application of new technology to overcome past limitations, and integration with nonbiological process steps.

In order to satisfy the demand for feedstocks for petrochemicals, it will be necessary to develop the reservoirs (of heavy oil) and deposits (of extra heavy oil and tar sand bitumen) that are predominantly located in the Western hemisphere (Chapter 2). These resources are more difficult and costly to extract, so they have barely been touched in the past. However, through these resources,
the world could soon have access to oil sources almost equivalent to those of the Middle East. In fact, with the variability and uncertainty of crude oil supply due to a variety of geopolitical issues (Speight, 2011b), investments in the more challenging reservoirs tend to be on a variable acceleration-deceleration slope.

Nevertheless, the importance of heavy oil, extra heavy oil, and tar sand bitumen will continue to emerge as the demand for crude oil products remains high. As this occurs, it is worth moving ahead with heavy oil, extra heavy oil, and tar sand bitumen resources on the basis of obtaining a measure (as yet undefined and country-dependent) of oil independence. These will lead eventually—hopefully sooner rather than later—to the adoption of coal, oil shale (produced from kerogen in shale formations), and renewable feedstocks as the source materials for the production of petrochemicals. The term *renewable feedstocks* includes a huge number of materials such as agricultural crops rich in starch, lignocellulosic materials (biomass), or biomass material recovered from a variety of processing wastes.

The general term *biomass* refers to any material derived from living organisms, usually plants. In contrast to depleting feedstocks such as natural gas and crude oil, the production of bio-based chemicals which can replace the petroleum-derived chemicals will prove to be a reliable supply of resources for the future. Existing chemical technology is continually being developed to provide chemicals and end products from biomass (Bozell, 1999; Besson et al., 2014; Straathof, 2014; Khoo et al., 2015).

For bioprocesses—the conversion of biomass into useful products such as fuels and petrochemicals—one opportunity that exists is the production of butanol from bioprocessing which could be a major commodity chemical that has application as a feedstock for such products as butyl butyrate. Also, chemicals such as xylose, xylitol, furfural, tetrahydrofuran, glucose, gluconic acid, sorbitol, mannitol, levulinic acid, and succinic acid are materials that could be prepared from inexpensive cellulose and hemicellulose-derived sugars, available from clean biomass fractionation. As further examples, (i) anthraquinone, a well-known pulping catalyst and chemical intermediate, can be prepared from lignin while butadiene and a variety of pentane derivatives can be prepared using fast pyrolysis followed by catalytic upgrading on zeolite-type catalysts; (ii) acetic acid can be produced. From synthesis gas, a route that appears to be an interesting match given the unique composition of synthesis gas available from biomass, and makes possible a balanced process (through intermediate methanol or ethanol) without the costs of reforming the synthesis gas; and (iii) peracetic acid is an oxidant that is a good non-chlorine-containing pulp bleaching agent which would permit market penetration of this chemical into the pulp and paper industry.

However, a basic understanding of reactions for selectively converting biomass and biomass-derived materials into chemicals is needed. A fundamental understanding of new catalytic processes for selectively manipulating and modifying carbohydrates, lignin, and other biomass fractions will greatly improve the ability to bring biomass-derived products to market. The behavior of oxygenated molecules on zeolite and other shape-selective catalysts could lead to a better design of processes for chemicals from biomass. Developing special catalysts for biomass processing is not a high priority for the chemicals industry, but is essential for this new field if it is to compete with petroleum resources and cost-effectively produce fuels and chemicals.

Consequently, there is a renewed interest in the utilization of plant-based matter as a raw material feedstock for the chemicals industry. Plants accumulate carbon from the atmosphere via photosynthesis and the widespread utilization of these materials as basic inputs into the generation of power, fuels and chemicals is a viable route to reduce greenhouse gas emissions. As a result, the petroleum and petrochemical industries are coming under increasing pressure not only to compete effectively with global competitors utilizing more advantaged hydrocarbon feedstocks, but also to ensure that its processes and products comply with increasingly stringent environmental legislation.

Reducing dependence of any country on imported crude oil is of critical importance for long-term security and continued economic growth. Supplementing petroleum consumption with renewable biomass resources is a first step toward this goal. The realignment of the chemical industry
from one of the petrochemical refining to a biorefinery concept, given time, feasibly has become a national goal of many oil-importing countries. However, clearly defined goals are necessary for construction of a biorefinery and increasing the use of biomass-derived feedstocks in industrial chemical production is important to keep the goal in perspective (Clark and Deswarte, 2008). In this context, the increased use of biofuels should be viewed as one of a range of possible measures for achieving self-sufficiency in energy, rather than a panacea (Crocker and Crofcheck, 2006). Thus, in any text about the production of chemicals (petrochemicals), it would be a remiss to omit other sources of chemicals such as coal and biomass.

3.2 COAL

Coal, which is currently considered the bad boy of fossil fuels due to environmental issues some of which are real and some of which are emotional, may become more important both as an energy source and as the source of organic chemical feedstock in the 21st century.

The chemicals-from-coal industry was born in the late 18th century at the time of the Industrial Revolution when power and chemicals from coal were everyday occurrences. Thus, the coal chemicals industry refers to the conversion of coal into gas, liquid, solid fuels, and chemicals after chemical processing with coal as raw material. In the early days of the chemicals-from-coal industry, the term chemicals covered primarily ammonia, hydrocarbon gases, low-boiling aromatic derivatives (benzene, toluene, and xylene (BTX)), difficult-to define tar acids, difficult-to define tar bases, tar, pitch, and coke. In the United States, these chemicals were derived from coal almost exclusively through high-temperature byproduct carbonization. In England and Europe, these and other chemicals have been obtained to some extent through various low-temperature carbonization processes and by coal hydrogenation in England and Germany (Speight, 2013a).

Thus, the processes for the production of chemicals from coal were predominantly coking, gasification, liquefaction of coal, as well as coal tar processing, and carbide acetylene chemical engineering. The significant time frame for the production of chemicals from coal was the period from 1920 to 1940 after which World War II brought imperative demands for toluene, ammonia, and other chemicals that could not be met by the coke plants. Petroleum and natural gas were used as raw materials, and since that time they have dominated the chemical industry. However, as natural gas and crude oil resources of the world decrease (they are, of course, nonrenewable resources), the chemicals-from-coal industry may once again realize broad prospects for development. This must go along with the realization that emissions from coal plants can be reduced significantly by the installation of emissions reduction processes that have now been placed into operation in the coal-generated power plants.

In the production technology of coal processing and utilization, coking process technology is one of the earliest applications, and it is still an important part of the chemical industry. Coal gasification occupies an important position in the coal chemical industry and is used in the production of various types of gas fuel. It is a clean energy and is conducive to the improvement of living standards and environmental protections. Synthetic gas produced by coal gasification is the raw material of many products such as synthetic liquid fuel, and raw materials for the production of chemicals. The direct coal liquefaction (high-pressure coal hydrogenation liquefaction for production of naphtha and kerosene) and indirect coal liquefaction (through gasification of coal for synthesis of gasoline and diesel) can produce synthetic petroleum and chemical products (Owen, 1981; Speight, 2013a).

In fact, coal has several positive attributes when considered as a feedstock for aromatic chemicals, specialty chemicals, and carbon-based materials. Substantial progress in advanced polymer materials, incorporating aromatic and polyaromatic units in their main chains, has created new opportunities for developing value-added or specialty organic chemicals from coal and tars from coal carbonization for coke making. The decline of the coal tar industry has diminished the traditional sources of these chemicals. A new coal chemistry for chemicals and materials from coal may involve direct and indirect coal conversion strategies as well as the coproduction approach.
In addition, the needs for environmental-protection applications have also expanded market demand for carbon materials and carbon-based adsorbents.

### 3.2.1 Coal Feedstocks

By way of introduction, coal is a natural combustible rock composed of an organic heterogeneous substance contaminated with variable amounts of inorganic compounds. Coal is classified into different ranks according to the degree of chemical change that occurred during the decomposition of plant remains in the prehistoric period. In general, coals with a high heating value and high fixed carbon content are considered to have been subjected to more severe changes than those with lower heating values and fixed carbon contents. For example, peat, which is considered a young coal, has a low fixed carbon content and a low heating value. Important coal ranks are anthracite (which has been subjected to the most chemical change and is mostly carbon), bituminous coal, subbituminous coal, and lignite.

The birth of coal chemical industry first appeared in the late 18th century, and in the 19th century the complete system of coal chemical industry was set up. After entering 20th century, raw materials of organic chemicals were changed into coal from the former agricultural and forestry products, and then coal chemical industry became an important part of chemical industry. After World War II, the petrochemical industry saw rapid development, which weakened the position taken up by coal chemical industry by changing raw materials from coal to petroleum and natural gas. The organic matters and chemical structures of coal with condensed rings as their core units connected by bridged bonds can transform coal into various fuels and chemical products through hot working and catalytic processing.

Coal carbonization is the earliest and most important method. Coal carbonization is mainly used to produce cokes for metallurgy and some secondary products like coal gas, benzene, methylbenzene, etc. Coal gasification takes up an important position in chemical industry. City gas and varieties of fuel gases can be produced by coal gasification. The common role of low-temperature carbonization, direct coal liquefaction and indirect coal liquefaction is to produce liquid fuels.

Thus, for many years, chemicals that have been used for the manufacture of such diverse materials as nylon, styrene, fertilizers, activated carbon, drugs, and medicine, as well as many others have been made from coal (Gibbs, 1961; Mills, 1977; Pitt and Millward, 1979). These products will expand in the future as petroleum and natural gas resources become strained to supply petrochemical feedstocks and coal becomes a predominant chemical feedstock once more. Although many traditional markets for coal tar chemicals have been taken over by the petrochemical industry, the position can change suddenly as oil prices fluctuate upwards. Therefore, the concept of using coal as a major source of chemicals can be very real indeed.

A complete description of the processes to produce all the possible chemical products is beyond the scope of this text. In fact, the production of chemicals from coal has been reported in numerous texts; therefore, it is not the purpose of this text to repeat these earlier works. It is, however, the goal of this chapter to present indications of the extent to which chemicals can be produced from coal as well as indications of the variety of chemical types that arise from coal (e.g., see Lowry, 1945; Speight, 2013a).

On the basis of the thermal chemistry of coal (Speight, 2013a), many primary products of coal reactions are high molecular weight species, often aromatic in nature, that bear some relation to the carbon skeletal of coal. The secondary products (i.e., products formed by decomposition of the primary products) of the thermal decomposition of coal are lower molecular weight species but are less related to the carbon species in the original coal as the secondary reaction conditions become more severe (higher temperatures and/or longer reaction times).

In very general terms, it is these primary and secondary decomposition reactions of coal which are the means to produce chemical from coal. There is some leeway in terms of choice of the reaction conditions, and there is also the option of the complete decomposition of coal (i.e., gasification)
and the production of chemicals from the synthesis gas (a mixture of carbon monoxide, CO, and hydrogen, H₂) produced by the gasification process (Chapter 5) (Speight, 2013a).

### 3.2.2 Properties and Composition

Coal is a combustible dark brown to black organic sedimentary rock that occurs in coalbeds or coal seams. Coal is composed primarily of carbon with variable amounts of hydrogen, nitrogen, oxygen, and sulfur and may also contain mineral matter and gases as part of the coal matrix. Coal begins as layers of plant matter that has accumulated at the bottom of a body of water after which, through anaerobic metamorphic processes, changes the chemical and physical properties of the plant remains occurred to create a solid material.

Coal is the most abundant fossil fuel in the United States, having been used for several centuries and occurs in several regions. Knowledge of the size, distribution, and quality of the coal resources is important for governmental planning; industrial planning and growth; the solution of current and future problems related to air, water, and land degradation; and for meeting the short- and long-term energy needs of the country. Knowledge of resources is also important in planning for the exportation and importation of fuel.

The types of coal, in increasing order of alteration, are lignite (brown coal), subbituminous, bituminous, and anthracite. It is believed that coal starts off as a material that is closely akin to peat, which is metamorphosed (due to thermal and pressure effects) to lignite. With the further passing of time, lignite increases in maturity to subbituminous coal. As this process of burial and alteration continues, more chemical and physical changes occur and the coal is classified as bituminous. At this point the coal is dark and hard. Anthracite is the last of the classifications, and this terminology is used when the coal has reached ultimate maturation.

The degree of alteration (or metamorphism) that occurs as a coal matures from peat to anthracite is referred to as the rank of the coal, which is the classification of a particular coal relative to other coals, according to the degree of metamorphism, or progressive alteration, in the natural series from lignite to anthracite (ASTM D388). This method of ranking coals used in the United States and Canada was developed by the American Society for Testing and Materials (ASTM; now ASTM International) and are: (i) heating value, (ii) volatile matter, (iii) moisture, (iv) ash production by combustion which is reflective of the mineral matter content, and (v) fixed carbon (Speight, 2005, 2013a).

Low-rank coal (such as lignite) has lower energy content because they have low carbon content. They are lighter (earthier) and have higher moisture levels. As time, heat, and burial pressure all increase, the rank does as well. High-rank coals, including bituminous and anthracite coals, contain more carbon than lower-rank coals which results in a much higher energy content. They have a more vitreous (shiny) appearance and lower moisture content then lower-rank coals.

There are many compositional differences between the coals mined from the different coal deposits worldwide. The different types of coal are most usually classified by rank which depends upon the degree of transformation from the original source (i.e., decayed plants) and is therefore a measure of a coal’s age. As the process of progressive transformation took place, the heating value and the fixed carbon content of the coal increased and the amount of volatile matter in the coal decreased.

### 3.2.3 Conversion

The thermal properties of coal are important in determining the applicability of coal to a variety of conversion processes. For example, the heat content (also called the heating value or calorific value) (Chapter 8) is often considered to be the most important thermal property. However, there are other thermal properties that are of importance insofar as they are required for the design of equipment that is to be employed for the utilization (conversion, thermal treatment) of coal in processes such as combustion, carbonization, gasification, and liquefaction (Speight, 2013).
The thermal decomposition (which includes pyrolysis processes and carbonization processes) often may be used interchangeably. However, it is more usual to apply the term pyrolysis (a thermochemical decomposition of coal or organic material at elevated temperatures in the absence of oxygen which typically occurs under pressure and at operating temperatures above 430°C (800°F)) to a process which involves widespread thermal decomposition of coal (with the ensuing production of a char—carbonized residue).

The term carbonization is more correctly applied to the process for the production of char or coke when the coal is heated at temperatures in excess of 500°C (930°F). The ancillary terms volatilization and distillation are also used from time to time but more correctly refer to the formation and removal of volatile products (gases and liquids) during the thermal decomposition process. Thus, carbonization is the destructive distillation of coal in the absence of air accompanied by the production of carbon (coke) as well as the production of liquid and gaseous products. Next to combustion, carbonization represents one of the most popular, and oldest, uses of coal. The thermal decomposition of coal on a commercial scale is often more commonly referred to as carbonization and is more usually achieved by the use of temperatures up to 1,500°C (2,730°F). The degradation of the coal is quite severe at these temperatures and produces (in addition to the desired coke) substantial amounts of gaseous products.

Coal liquefaction is a process used to convert coal, a solid fuel, into a substitute for liquid fuels such as diesel and gasoline. Coal liquefaction has historically been used in countries without a secure supply of petroleum, such as Germany (during World War II) and South Africa (since the early 1970s). The technology used in coal liquefaction is quite old, and was first implemented during the 19th century to provide gas for indoor lighting. Coal liquefaction may be used in the future to produce oil for transportation and heating, in case crude oil supplies are ever disrupted.

The production of liquid fuels from coal is not new and has received considerable attention. In fact, the concept is often cited as a viable option for alleviating projected shortages of liquid fuels as well as offering some measure of energy independence for those countries with vast resources of coal who are also net importers of crude oil.

The gasification of coal or a derivative (i.e., char produced from coal) is, essentially, the conversion of coal (by any one of a variety of processes) to produce combustible gases (Speight, 2013). With the rapid increase in the use of coal from the 15th century onwards, it is not surprising that the concept of using coal to produce a flammable gas, especially the use of the water and hot coal, became commonplace. In fact, the production of gas from coal has been a vastly expanding area of coal technology, leading to numerous research and development programs. As a result, the characteristics of rank, mineral matter, particle size, and reaction conditions are all recognized as having a bearing on the outcome of the process; not only in terms of gas yields but also on gas composition and properties. In fact, the products of coal gasification are varied insofar as the gas composition varies with the system employed. Furthermore, it is emphasized that the gas product must be first freed from any pollutants such as particulate matter and sulfur compounds before further use, particularly when the intended use is a water-gas shift or methanation as might be necessary in the coal-to-gas-to-chemicals industry.

In terms of coal use through conversion processes, serious efforts have been made to reduce the environmental footprint left by such processes by the initiation of the Clean Coal Technology Demonstration Program that has laid the foundation for effective technologies now in use that have helped significantly lower emissions of sulfur dioxide (SO₂), nitrogen oxides (NOₓ), and airborne particulates. The term clean coal technology refers to a new generation of advanced coal utilization technologies that are environmentally cleaner and in many cases more efficient and less costly than the older, and more conventional coal-using processes (Speight, 2013). Clean coal technologies offer the potential for a more clean use of coal which will have a direct effect on the goal of the reduction of emissions and process waste into the environment thereby making a positive contribution to the resolution of issues relating to acid rain and global climate change.
3.2.4 COAL TAR CHEMICALS

The coal carbonization industry was established initially as a means of producing coke (Chapter 16) but a secondary industry emerged (in fact, became necessary) to deal with the secondary or byproducts (namely, gas, ammonia liquor, crude benzole, and tar) produced during carbonization (Table 3.1) (Speight, 2013a).

Coal tar is a byproduct of the carbonization of coal to produce coke and/or natural gas. Physically, coal tar is black or dark brown-colored liquid or a high-viscosity semisolid which is one of the byproducts formed when coal is carbonized (Speight, 2013a). Coal tar usually takes the form of a viscous liquid or semisolid with a naphthalene-like odor. Chemically, coal tar is a complex combination of polycyclic aromatic hydrocarbon (PAH, often represented as PNA as well) derivatives, phenol derivatives, heterocyclic oxygen, sulfur, and nitrogen compound derivatives. Because of its flammable composition coal tar is often used for fire boilers, in order to create heat. Before any heavy oil flows easily they must be heated.

Coal tar, coal tar pitch, and coal tar creosote are very similar mixtures obtained from the distillation of coal tars. The physical and chemical properties of each are similar, although limited data are available for coal tar, and coal tar pitch. By comparison, coal tar creosote is a distillation product of coal tar. They have an oily liquid consistency and range in color from yellowish-dark green to brown. The coal tar creosotes consist of aromatic hydrocarbon derivatives, anthracene, naphthalene, and phenanthrene derivatives. Typically, polycyclic aromatic hydrocarbon derivatives—two-ring naphthalene derivatives and higher condensed ring derivatives—constitute the majority of the creosote mixture. Unlike the coal tar and coal tar creosote, coal tar pitch is the nonvolatile residue produced during the distillation of coal tar. The pitch is a shiny, dark brown to black residue that contains polycyclic aromatic hydrocarbon derivatives and their methyl and polymethyl derivatives, as well as heteronuclear compounds.

As an aside, the nomenclature of the coal tar industry, like that of the petroleum industry (Speight, 2014, 2017), needs refinement and clarification. Almost any black, undefined, semisolid-to-liquid material is popularly, and often incorrectly, described as tar or pitch whether it be a manufactured product or a naturally occurring substance (Chapter 16). However, to be correct and to avoid any ambiguity, use of these terms should be applied with caution. The term “tar” is usually applied to the volatile and nonvolatile soluble products that are produced during the carbonization, or destructive distillation (thermal decomposition with the simultaneous removal of distillate), of various organic materials. By way of further definition, distillation of the tar yields an oil (volatile organic products often referred to as benzole) and a nonvolatile pitch. In addition, the origin of the tar or pitch should be made clear by the use of an appropriate descriptor, i.e., coal tar, wood tar, coal tar pitch, and the like.

Thus, the eventual primary products of the carbonization process (Chapter 16) are coke, coal tar, and crude benzole (which should not be mistaken for benzene although benzene can be isolated from benzole), ammonia liquor, and gas. The benzole fraction contains a variety of compounds, both aromatic and aliphatic in nature and can be conveniently regarded as an analog of petroleum naphtha (Speight, 2014).

<table>
<thead>
<tr>
<th>TABLE 3.1</th>
<th>Bulk Products (% w/w) from Coal Carbonization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>Low-temperature Carbonization</td>
</tr>
<tr>
<td>Gas</td>
<td>5</td>
</tr>
<tr>
<td>Liquids</td>
<td>15</td>
</tr>
<tr>
<td>Tar</td>
<td>10</td>
</tr>
<tr>
<td>Coke</td>
<td>70</td>
</tr>
</tbody>
</table>
The yield of byproduct tar from a coke oven is, on average, 8.5–9.5 U.S. gallons (32–36 L) per ton of coal carbonized but the yield from a continuous vertical retort is approximately 15.5–19.0 U.S. gallons (60–75 L) per ton of coal carbonized. In low-temperature retorts, the yield of tar varies over the range 19.0–36.0 U.S. gallons (75–135 L) per ton of coal.

Crude coal tar sometimes referred to as crude coke oven tar or simply coal tar is a byproduct collected during the carbonization of coal to make coke. Coke is used as a fuel and as a reducing agent in smelting iron ore in a blast furnace to manufacture steel and in foundry operations. Crude coal tar is a raw material that is further distilled to produce various carbon products, refined tars, and oils used as essential components in the production of aluminum, rubber, concrete, plasticizers, coatings, and specialty chemicals. Crude coal tars have been processed in the United States since Koppers Company completed the first byproduct coke ovens around 1912.

During the distillation of crude coal tar, low-density oil and medium-density oil are removed from the crude coal tar to produce various refined coal tar products. These low-density and medium-density oils represent 20–50% w/w of the crude coal tar depending upon the refined product that is desired. Coal tar contains hundreds of chemical compounds that will have varying amounts of polycyclic aromatic hydrocarbon derivatives depending upon the source.

Refined tar-based coatings have a great advantage over asphalt in that it has better chemical resistance than asphalt coatings. Refined tar-based coatings hold up better under exposures of petroleum oils and inorganic acids. Another outstanding quality of refined tar-based coatings is their extremely low permeability to moisture and there high dielectric resistance, both of which contribute to the corrosion resistance. (Munger, 1984).

Coal tar is a complex mixture and the components range from low-boiling, low molecular weight species, such as benzene, to high molecular weight polynuclear aromatic compounds. Similar classes of chemical compounds occur in the tars, usually with little regard to the method of manufacture, but there are marked variations in the proportions present in the tars due to the type of coal, the type of carbonizing equipment, and the method of recovery (Chapter 16).

Coke oven tar contains relatively low proportions (ca. 3%) of tar acids (phenols), vertical retort tars may contain up to 30% phenolic compounds. Moreover, the phenols in coke oven tars mainly comprise phenol, methyl and poly-methyl phenols (e.g. cresols and xylenols) and naphthols; those in vertical retort tar are mainly xylenols and higher-boiling phenols.

Coke oven tars contain only minor quantities of non-aromatic hydrocarbon derivatives, whilst the vertical retort tars may have up to 6% of paraffinic compounds. Low-temperature tars are more paraffinic and phenolic (as might be expected from relative lack of secondary reactions) than are the continuous vertical retort tars. Coke oven tars are comparatively rich in naphthalene and anthracene and distillation is often the means by which various chemicals can be recovered from these particular products. On the other hand, another objective of primary distillation is to obtain a pitch or refined-tar residue of the desired softening point. If the main outlet for the pitch is as a briquetting (Chapter 17) or electrode binder, primary distillation is aimed at achieving a medium-soft pitch as product or for the production of road asphalt.

In terms of composition, the compounds positively identified as pitch components consist predominantly of condensed polynuclear aromatic hydrocarbon derivatives or heterocyclic compounds containing three to six rings. Some methyl and hydroxyl substituent groups have also been observed, and it is reasonable to assume that vertical retort pitches contain paraffinic constituents in addition (McNeil, 1966). Pitches are often characterized by solvent analysis and many specifications quote limits for the amounts insoluble in certain solvents (Hoiberg, 1966).

Primary distillation of crude tar produces pitch (nonvolatile residue) and several distillate fractions, the amounts and boiling ranges of which are influenced by the nature of the crude tar (which depends upon the coal feedstock) and the processing conditions. For example, in the case of the tar from continuous vertical retorts, the objective is to concentrate the tar acids (phenol, cresols, and xylenols) into carbolic oil fractions. On the other hand, the objective with coke oven tar is to
concentrate the naphthalene and anthracene components into naphthalene oil and anthracene oil, respectively.

The products of tar distillation can be divided into refined products, made by the further processing of the fractions, and bulk products which are pitch, creosote, and their blends. Coal tar low-boiling oil, or crude benzole, is similar in chemical composition to the crude benzole recovered from the carbonization gases at gas works and in coke oven plants. The main components are benzene, toluene, and xylene(s) with minor quantities of aromatic hydrocarbon derivatives, paraffins, naphthenes (cyclic aliphatic compounds), phenols, as well as sulfur and nitrogen compounds.

The first step in refining benzole is steam distillation is employed to remove compounds boiling below benzene. Low-boiling naphtha and high-boiling naphtha are the mixtures obtained when the 150°C–200°C (300°F–390°F) fraction, after removal of tar acids and tar bases, is fractionated. These naphtha fractions are used as solvents. To obtain pure products, the benzole can be distilled to yield a fraction containing benzene, toluene, and xylene(s). Benzene is used in the manufacture of numerous products including nylon, gammexane, polystyrene, phenol, nitrobenzene, and aniline. On the other hand, toluene is a starting material in the preparation of saccharin, trinitrotoluene, and polyurethane foams. The xylenes present in the low-boiling oil are not always separated into the individual pure isomers since xylene mixtures can be marketed as specialty solvents. Higher-boiling fractions of the distillate from the tar contain pyridine bases, naphtha, and coumarone resins. Other tar bases occur in the higher-boiling range and these are mainly quinoline, isoquinoline, and quinaldine.

Pyridine has long been used as a solvent, in the production of rubber chemicals, textile water-repellant agents and in the synthesis of drugs. The derivatives 2-benzylpyridine and 2-aminopyridine, are used in the preparation of antihistamines. Another market for pyridine is in the manufacture of the nonpersistent herbicides diquat and paraquat.

Alpha-picoline (C₆H₇N, 2-picoline; 2-methylpyridine) is used for the production of 2-vinylpyridine which, when copolymerized with 1,4-butadiene (CH₂=CHCH=CH₂) and styrene (C₆H₅CH=CH₂), produces a used as a latex adhesive which is used in the manufacture of automobile tires.

Other uses are in the preparation of 2-β-methoxyethyl pyridine (known as Promintic, an anthelmintic for cattle) and in the synthesis of a 2-picoline quaternary compound (Amprolium) which is used against coccidiosis in young poultry. Beta-picoline (3-picoline; 3-methylpyridine) can be oxidized to nicotinic acid, which with the amide form (nicotinamide), belongs to the vitamin B complex; both products are widely used to fortify human and animal diets. γ-Picoline (4-picoline, 4-methylpyridine) is an intermediate in the manufacture of isonicotinic acid hydrazide (Isoniazide) which is a tuberculostatic drug. The 2,6-Lutidine (2,6-dimethylpyridine) can be converted to dipicolinic acid, which is used as a stabilizer for hydrogen peroxide and peracetic acid.

The tar-acid free and tar-base free coke oven naphtha can be fractionated to give a narrow boiling fraction (170°C–185°C; 340°F–365°F) containing coumarone and indene. This is treated with
strong sulfuric acid to remove unsaturated components and is then washed and redistilled. The concentrate is heated with a catalyst (such as a boron fluoride/phenol complex) to polymerize the indene and part of the coumarone. Unreacted oil is distilled off and the resins obtained vary from pale amber to dark brown in color. They are used in the production of flooring tiles and in paints and polishes.

Naphthalene and several tar acids are the important products extracted from volatile oils from coal tar. It is necessary to first extract the phenolic compounds from the oils and then to process the phenol-depleted oils for naphthalene recovery. Tar acids are produced by extraction of the oils with aqueous caustic soda at a temperature sufficient to prevent naphthalene from crystallizing. The phenols react with the sodium hydroxide to give the corresponding sodium salts as an aqueous extract known variously as crude sodium phenate, sodium phenolate, sodium carbolate, or sodium cresylate. The extract is separated from the phenol-free oils which are then taken for naphthalene recovery.

Phenol (C₆H₅OH) is a key industrial chemical; however, the output of phenol from coal tar is exceeded by that of synthetic phenol. Phenol is used for the production of phenol-formaldehyde resins, while other important uses in the plastic field include the production of polyamides such as nylon, of epoxy resins and polycarbonates based on bisphenol A and of oil-soluble resins from p-t-butyl and p-octyl phenols. Phenol is used in the manufacture of pentachlorophenol which is used as a fungicide and in timber preservation. Aspirin and many other pharmaceuticals, certain detergents, and tanning agents are all derived from phenol, and another important use is in the manufacture of 2,4-dichlorophenoxyacetic acid (2,4-D) which is a selective weed killer.

![2,4-Dichlorophenoxyacetic acid](image)

Orthocresol has been used predominantly for the manufacture of the selective weed killers: 4-chloro-2-methyl-phenoxyacetic acid (MCPA) and the corresponding propionic acid (MCPP) and the butyric acid (MCPB) as well as 2,4-dinitro-o-cresol (DNOC), a general herbicide/insecticide.

![4-chloro-2-methyl-phenoxyacetic acid (MCPA)](image)

2,4-dinitro-o-cresol (DNOC)

Paracresol (p-HOC₆H₄CH₃) has been used widely for the manufacture of BHT (2,6-ditertiarybutyl-4-hydroxytoluene), an antioxidant.
Coal, Oil Shale, and Biomass

Metacresol and paracresol mixtures are used in the production of phenoplasts, tritolyl phosphate plasticizers and petroleum additives.

Other outlets for cresylic acids are as agents for froth flotation, metal degreasing, as solvents for wire-coating resins, antioxidants, cutting oils, nonionic detergents, and disinfectants.

Naphthalene is probably the most abundant component in high-temperature coal tars. The primary fractionation of the crude tar concentrates the naphthalene into oils which, in the case of coke oven tar, contain the majority (75–90% w/w) of the total naphthalene. After separation, naphthalene can be oxidized to produce phthalic anhydride which is used in the manufacture of alkyd and glyptal resins and plasticizers for polyvinyl chloride and other plastics.

The main chemical extracted on the commercial scale from the higher-boiling oils (b.p. 250°C, 480°F) is crude anthracene. The majority of the crude anthracene is used in the manufacture of dyes after purification and oxidation to anthraquinone.

Coal tar creosote is the residual distillate oils obtained when the valuable components, such as naphthalene, anthracene, tar acids, and tar bases have been removed from the corresponding fractions (Figure 3.1). It is a brownish-black/yellowish-dark green oily liquid with a characteristic sharp odor, obtained by the fractional distillation of crude coal tars. The approximate distillation range is 200°C–400°C (390°F–750°F). The chemical composition of creosotes is influenced by the origin of the coal and also by the nature of the distilling process; as a result, the creosote components are rarely consistent in their type and concentration.

Major uses for creosotes have been as a timber preservative, as fluxing oils for pitch and bitumen, and in the manufacture of lamplblack and carbon black. However, the use of creosote as a timber preservative has recently come under close scrutiny, as have many other ill-defined products of coal processing. Issues related to the seepage of such complex chemical mixtures into the surrounding environment have brought an awareness of the potential environmental and...
3.3 OIL SHALE

Oil shale represents a large and mostly untapped hydrocarbon resource. Like tar sand (oil sand in Canada) and coal, oil shale is considered unconventional because oil cannot be produced directly from the resource by sinking a well and pumping. Oil has to be produced by thermal decomposition of the organic matter (kerogen) in the shale. The organic material contained in the shale is called kerogen, a solid material intimately bound within the mineral matrix. However, oil shale does not contain any oil—this must be produced by a process in which the kerogen is thermally decomposed (cracked) to produce the liquid product (shale oil) (Scouten, 1990; Lee, 1991; Lee et al., 2007; Speight, 2008). Compared to crude oil, shale oil obtained by retorting of oil shale is characterized by wide boiling range and by large concentrations of heteroelements and also by high content of oxygen-, nitrogen-, or sulfur-containing compounds.

3.3.1 SHALE OIL PRODUCTION

Shale oil is produced from oil shale by the thermal decomposition of the kerogen component of oil shale. Oil shale must be heated to temperatures between 400°C and 500°C (750°F–930°F). This heating process is necessary to convert the embedded sediments to kerogen oil and combustible gases. Generally, with solid fossil fuels, the yield of the volatile products depends mainly on the hydrogen content in the convertible solid fuel. Thus, compared with coal, oil shale kerogen contains more hydrogen and can produce relatively more oil and gas when thermally decomposed (Speight, 2008, 2012, 2013). From the standpoint of shale oil as a substitute for petroleum products, the composition is of great importance.
The thermal processing of oil shale to oil has quite a long history and various facilities and technologies have been used including mining of the shale followed by thermal processing as well as in situ decomposition of the shale (Speight, 2008, 2012). In principle, there are two ways of accomplishing the thermal decomposition of the kerogen in the shale: (i) low-temperature processing—semicoking or retorting—by heating the oil shale up to about 500°C (930°F), and (ii) high-temperature processing—coking—heating up to 1,000°C–1,200°C (1,830°F–2,190°F). A high yield deposit of oil shale will yield 25 gallons of oil per ton of oil shale.

In the mining-thermal processing option (ex situ production), oil shale is mined, crushed, and then subjected to thermal processing at the surface in an oil shale retort. Both pyrolysis and combustion have been used to treat oil shale in a surface retort. In the second option (in situ production), the shale is left in place and the retorting (e.g., heating) of the shale occurs in the ground. Generally, surface processing consists of three major steps: (i) oil shale mining and ore preparation, (ii) pyrolysis of oil shale to produce kerogen oil, and (iii) processing kerogen oil to produce refinery feedstock and high-value chemicals. For deeper, thicker deposits, not as amenable to surface or deep-mining methods, shale oil can be produced by in situ technology. In situ processes minimize, or in the case of true in situ, eliminate the need for mining and surface pyrolysis, by heating the resource in its natural depositional setting.

Depending on the depth and other characteristics of the target oil shale deposits, either surface mining or underground mining methods may be used. Each method, in turn, can be further categorized according to the method of heating. Another way in which the various retorting processes differ is the manner by which heat is provided to the shale by hot gas—(i) by a solid heat carrier or (ii) by conduction through a heated wall. After mining, the oil shale is transported to a facility for retorting after which the oil must be upgraded by further processing before it can be sent to a refinery, and the spent shale must be disposed, often by putting it back into the mine. Eventually, the mined land is reclaimed. Both mining and processing of oil shale involve a variety of environmental impacts, such as global warming and greenhouse gas emissions, disturbance of mined land, disposal of spent shale, use of water resources, and impacts on air and water quality.

3.3.2 Shale Oil Properties

Shale oil is a synthetic crude oil produced by retorting oil shale and is the pyrolysis product of the organic matter (kerogen) contained in oil shale. The raw shale oil produced from retorting oil shale can vary in properties and composition (Scouten, 1990; Lee, 1991; Lee et al., 2007; Speight, 2008). Compared with petroleum, shale oil is high in nitrogen and oxygen compounds and a higher specific gravity—on the order of 0.9–1.0 owing to the presence of high-boiling nitrogen-, sulfur-, and oxygen-containing compounds. Shale oil also has a relatively high pour point and small quantities of arsenic and iron are present.

The chemical potential of oil shale as retort fuel to produce shale oil and from that liquid fuel and specialty chemicals has been used so far to a relatively small extent. Using stepwise cracking, various liquid fuels have been produced and even exported before World War II. At the same time, shale oils possess molecular structures of interest to the specialty chemicals industry and also a number of nonfuel specialty products have been marketed based on functional group, broad range concentrate, or even pure compound values.

Shale oil (produced from kerogen-containing shale rock) is a complex mixture of hydrocarbon derivatives, and it is characterized using bulk properties of the oil. Shale oil usually contains large quantities of olefin derivatives and aromatic hydrocarbon derivatives as well as significant quantities of heteroatom compounds (nitrogen-containing compounds, oxygen-containing compounds, and sulfur-containing compounds). A typical shale oil composition includes: nitrogen 1.5–2% w/w, oxygen 0.5–1% w/w, and sulfur 0.15–1% w/w as well as mineral particles and metal-containing compounds (Scouten, 1990; Lee, 1991; Lee, 1991; Lee et al., 2007; Speight, 2008). Generally, the oil is less fluid than crude oil, which is reflected in the pour point that is in the order of 24°C–27°C.
(75°F–81°F), while conventional crude oil has a pour point in the order of –60°C to +30°C (–76°F to +86°F), which affects the ability of shale oil to be transported using unheated pipelines. Shale oil also contains polycyclic aromatic hydrocarbon derivatives.

Based on large quantities of oxygen-containing compounds in the high-boiling fraction, asphalt-blending material, road asphalt, construction mastics, anticorrosion oils, rubber softeners, benzene, and toluene for production of benzoic acid as well as solvent mixtures on pyrolysis of lower-boiling fractions of shale oil are produced. Higher-boiling (mid-distillate) shale oil fractions having antibiotic properties are used to produce effective oil for the impregnation of wood as a major shale oil-derived specialty product. Water-soluble phenols are selectively extracted from shale oil, fractionated and crystallized for production of pure 5-methylresorcinol and other alkyl resorcinol derivatives and high-value intermediates to produce tanning agents, epoxy resins and adhesives, diphenyl ketone and phenol-formaldehyde adhesive resins, rubber modifiers, chemicals, and pesticides. Some conventional products such as coke and various distillate fuels are produced from shale oil as byproducts.

However, the presence of the polar constituents (containing nitrogen and oxygen functions, sulfur compounds are also issues worthy of consideration) can cause shale oil to be incompatible with conventional petroleum feedstocks and petroleum products (Speight, 2014). As a result, particular care must be taken to ensure that all the functions that cause such incompatibility are removed from the shale oil before it is blended with a conventional petroleum liquid.

### 3.3.2.1 Hydrocarbon Products

The fundamental structure of the organic matter in oil shale gives rise to significant quantities of waxes consisting of long normal alkanes and the alkanes are distributed throughout the raw shale oil. However, the composition of shale oil depends on the shale from which it was obtained as well as on the retorting method by which it was produced (Scouten, 1990; Lee, 1991; Lee et al., 2007; Speight, 2008). As compared with petroleum crude, shale oil is high-boiling, viscous, and is high in nitrogen and oxygen compounds.

Retorting processes, which use flash pyrolysis, produce more fragments containing high molecular weight and multi-ring aromatic structures. Processes that use slower heating conditions, with greater reaction times at low temperature 300°C–400°C (570°F–750°F), tend to produce higher concentrations of n-alkanes. Naphthene-aromatic compounds of intermediate boiling range (such as 200°C–400°C, 390°F–750°F) also tend to be formed with the slower heating processes.

Saturated hydrocarbon derivatives in the shale oil include n-alkane derivatives, iso-alkane derivatives, and cycloalkane derivatives, and the alkene derivatives consist of n-alkene derivatives, iso-alkene derivatives, and cycloalkene derivatives, while the main components of aromatic derivatives are monocyclic, bicyclic, and tricyclic aromatic derivatives and their alkyl-substituted homologues. There is a variation of the distribution of saturated hydrocarbon derivatives, alkene derivatives, and aromatic derivatives in the different boiling ranges of the shale oil product. Saturated hydrocarbon derivatives in the shale oil increase and the aromatic derivatives increase slightly with a rise in boiling range, while alkene derivatives decrease with a rise in boiling range.

A typical Green River shale oil contains 40% w/w hydrocarbon derivatives and 60% w/w heteroatomic organic compounds, which contain nitrogen, sulfur, and oxygen. The nitrogen occurs in ring compounds with nitrogen in the ring, e.g., pyridines, pyridines, pyrolines as well as in nitriles, and typically comprises 60% w/w of the heteroatomic organic components. Another 10% w/w of these components contains organically bound sulfur compounds, which exists in thiophenes as well as sulfides and disulfides. The remaining 30% w/w consists of oxygen-containing compounds, which occur as phenols and carboxylic acids.

Shale oil not only contains a large variety of hydrocarbon compounds (Table 3.2), but also has high nitrogen content compared to a nitrogen content of 0.2–0.3% w/w for a typical petroleum (Scouten, 1990; Lee, 1991; Lee et al., 2007; Speight, 2008). In addition, shale oil also has a high olein and diolefin content—constituents, which are not present in petroleum and which require
Coal, Oil Shale, and Biomass

attention during processing due to their tendency to polymerize and form gums and sediments (fuel line deposits). It is the presence of these olefin derivatives and diolefin derivatives, in conjunction with high nitrogen content, which gives shale oil the characteristic difficulty in refining. Crude shale oil also contains appreciable amounts of arsenic, iron, and nickel that interfere with refining.

Other characteristic properties of shale oils are: (i) high levels of aromatic compounds, deleterious to kerosene and diesel fractions, (ii) low hydrogen-to-carbon ratio, (iii) low sulfur levels, compared with most crude oils available in the world (though for some shale oils from the retorting of marine oil shale, high sulfur compounds are present), (iv) suspended solids (finely divided rock) typically due to entrainment of the rock in the oil vapor during retorting, and (v) low-to-moderate levels of metals. Thus, because of the characteristics of shale oil, further processes are needed to improve the properties of shale oil products. The basic unit operations in the oil refining are distillation, coking, hydrotreating, hydrocracking, catalytic cracking, and reforming. The process selected will largely depend on the availability of equipment and the individual economics of the particular refinery.

Although the content of asphaltene constituents and/or resin constituents in shale oil is low—shale oil being a distillate product—asphaltene constituents in shale oil may be unique since, in shale oil, it is high heteroatomic content that causes precipitation as an asphaltene fraction rather than high molecular weight—for example, the hydroxy-pyridine derivatives are insoluble in low molecular weight alkane solvents. The polarity of the nitrogen polycyclic aromatic constituents may also explain the specific properties of emulsification of water and metal complexes.

### 3.3.2.2 Nitrogen-Containing Compounds

Nitrogen compounds in shale oil render technological difficulties in the downstream processing of shale oil, in particular, poisoning of the refining catalysts. Such nitrogen compounds are all originated from the oil shale and the amount and types depend heavily on the geochemistry of oil shale deposits. Since direct analysis and determination of molecular forms of nitrogen-containing compounds in oil shale rock is very difficult, the analysis of shale oil that is extracted by retorting processes provides valuable information regarding the organo-nitrogen species in the oil shale.

The nitrogen content in the shale oil is relatively higher than in natural crude oil (Scouten, 1990; Lee, 1991; Lee et al., 2007; Speight, 2008). The nitrogen-containing compounds identified in shale oils can be classified as basic, weakly basic, and nonbasic. The basic nitrogen compounds in shale oils are pyridine, quinoline, acridine, amine, and their alkyl-substituted derivatives, the weakly basic ones are pyrrole, indole, carbazole and their derivatives, and the nitrile and amide homologues are the nonbasic constituents.

Most of these compounds are useful chemicals (Scouten, 1990; Lee, 1991; Lee et al., 2007; Speight, 2008), although some of them are believed to affect the stability of shale oil. Generally,
basic nitrogen accounts for about one-half of the total nitrogen, and is evenly distributed in the different boiling point fractions. Nitrogen compounds occur throughout the boiling ranges of the shale oil, but have a decided tendency to exist in high-boiling point fractions. Pyrrole-type nitrogen increases with a rise in the boiling point of the shale oil fractions. Porphyrins may occur in the high-boiling point fraction of the shale oil.

Of the nitrogen-containing compounds in the low-boiling (\(<350^\circ C <660^\circ F\)) shale oil fraction, the majority contain one nitrogen atom. Benzoquinoline derivatives, principally acridine and alkyl-substituted homologues, could not be present significantly in the lower-boiling shale oil fractions because the boiling point of benzoquinoline and its alkyl-substituted homologues is higher than 350°C (660°F).

Organic nitrogen-containing compounds in the shale oil poison the catalysts in different catalytic processes. They also contribute to stability problems during storage of shale oil products since they induce polymerization processes, which cause an increase in the viscosity and give rise to the odor and color of the shale oil product. The high nitrogen content of shale oil could contribute to the surface and colloidal nature of shale oil, which forms emulsions with water.

### 3.3.2.3 Oxygen-Containing Compounds

The oxygen content of shale oil is much higher than in natural petroleum. Low molecular weight oxygen compounds in shale oil are mainly phenolic constituents—carboxylic acids and nonacidic oxygen compounds such as ketones are also present. Low molecular phenolic compounds are the main acidic oxygen-containing compounds in the low-boiling fraction of the shale oil and are usually derivatives of phenol, such as cresol and poly-methylated phenol derivatives.

The oxygen content of petroleum is typically in the order of 0.1–1.0% w/w, whereas the oxygen contents in shale oils are much higher and vary with different shale oil (Scouten, 1990; Lee, 1991; Lee et al., 2007). In addition, the oxygen content varies in different boiling point fractions of the shale oil. In general, it increases as the boiling point increases, and most of the oxygen atoms are concentrated in the high-boiling point fraction.

Other oxygen-containing constituents of shale oil include small amounts of carboxylic acids and nonacidic oxygen-containing compounds with a carbonyl functional group such as ketones, aldehydes, esters, and amides are also present in the \(<350^\circ C (<660^\circ F)\) fraction of shale oil. Ketones in the shale oil mainly exist as 2- and 3-alkanones. Other oxygen-containing compounds in the low-boiling \(<350^\circ C, <660^\circ F\) fraction include alcohols, naphthol, and ether constituents.

### 3.3.2.4 Sulfur-Containing Compounds

Sulfur compounds in the shale oils include thiols, sulfides, thiophenes, and other miscellaneous sulfur compounds. Elemental sulfur is found in some crude shale oil but is absent in others.

Generally, the sulfur content of oil-shale distillates is comparable in weight percentage to crude oil (Scouten, 1990; Lee, 1991; Lee et al., 2007; Speight, 2008). Refiners will be able to meet the current 500 ppm requirement by increasing the existing capacity of their hydrotreatment units and adding new units. However, refineries may face difficulty in treating diesel to below 500 ppm. The remaining sulfur is bound in multi-ring thiophene-type compounds that prove difficult to hydrotreat because the molecular ring structure attaches the sulfur on two sides and, if alkyl groups are present, provides steric protection for the sulfur atom. Although these compounds occur throughout the range of petroleum distillates, they are more concentrated in the residuum.

### 3.4 BIOMASS

Increasing attention has been (and is being) given to the possibility of utilizing photosynthetically active plants as natural solar energy-capturing devices with the subsequent conversion of available plant energy into useful fuels or chemical feedstocks (Table 3.3) (Metzger, 2006; Biddy et al., 2016; Wu et al., 2016). Acquisition of biological raw materials for energy capture follows
TABLE 3.3
Examples of Chemicals Produced from Bio-Sources

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Butadiene</td>
<td>The building block for the production of polybutadiene and styrene-rubber and butadiene rubber, currently produced from petroleum as a byproduct of ethylene manufacturing; can be produced through multiple biomass conversion strategies for the production of a direct renewable butadiene replacement.</td>
</tr>
<tr>
<td>1,4-Butanediol</td>
<td>A building block for the production of polymers, solvents, and specialty chemicals; bio-derived butanediol is being produced on a commercial scale utilizing commodity sugars; can be produced by the conversion of succinic acid to 1,4-butanediol.</td>
</tr>
<tr>
<td>Ethyl lactate</td>
<td>A biodegradable solvent produced by the esterification of ethanol and lactic acid; primary use for ethyl lactate is as an industrial product—the properties and performance meet or exceed those of traditional solvents such as toluene, methyl ethyl ketone, and N-methylpyrrolidone in many applications; the starting materials used to make ethyl lactate, lactic acid, and ethanol, have a high potential to be made from lignocellulosic sugars.</td>
</tr>
<tr>
<td>Fatty alcohols</td>
<td>Also called detergent alcohols, are linear alcohols of 12 or more carbons, used primarily to produce anionic and nonionic surfactants for household cleaners, personal care; derivatized by ethoxylation, sulfation, or sulfonation before use; can be produced from tallow, vegetable oils, or petroleum; also have the potential to be produced from renewable sources by autotrophic and heterotrophic algae, or by the microbial fermentation of carbohydrates.</td>
</tr>
<tr>
<td>Furfural</td>
<td>A heterocyclic aldehyde, produced by the dehydration of xylose, a monosaccharide often found in large quantities in the hemicellulose fraction of lignocellulosic biomass; any material containing a large amount of pentose (five-carbon) sugars, such as arabinose and xylose, can serve as a raw material for furfural production; converted to furfuryl alcohol which is used for the production of foundry resins; the anticorrosion properties of furfuryl alcohol is useful in the manufacture of furan fiber-reinforced plastics for piping; a broad spectrum of industrial applications, such as the production of plastics, pharmaceuticals, agrochemical products, and nonpetroleum-derived chemicals; not produced from fossil feedstocks; may be for conversion to jet and diesel fuel blend stocks.</td>
</tr>
<tr>
<td>Glycerin</td>
<td>A polyhydric alcohol and is a main component of triglycerides found in animal fats and vegetable oil. The word “glycerin” generally applies to commercial products containing mostly glycerol; the word “glycerol” most often refers specifically to the chemical compound 1,2,3-propanetriol and to the anhydrous content in a glycerin product or in a formulation; glycerin is the main byproduct of biodiesel production. It is also generated in the oleochemical industry during soap production and is produced synthetically from propyl; biodiesel and soap production accounts for most current glycerin production; therefore, the overall supply of glycerin is driven primarily by the demand for these products; a feedstock for conversion to more valuable products, such as epichlorohydrin and succinic acid; emerging uses include animal feed and marine fuel.</td>
</tr>
<tr>
<td>Isoprene</td>
<td>The building block for polyisoprene rubber, styrene co-polymers, and butyl rubber; produced by aerobic bioconversion of carbohydrates.</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>An alpha-hydroxy acid with dual functional groups; most frequently occurring carboxylic acid in nature; produced by microbial fermentation of carbohydrates; used for applications in food, pharmaceuticals, personal care products, industrial uses, and polymers; polylactic acid has gained popularity for use in food packaging, disposable tableware, shrink wrap, and 3-D printers.</td>
</tr>
<tr>
<td>1,3-Propanediol</td>
<td>A linear aliphatic diol, which makes it a useful chemical building block; can be used for a variety of applications including polymers, personal care products, solvents, and lubricants; also used as a component in poly trimethylene terephthalate polymers which are used in textiles and fibers.</td>
</tr>
</tbody>
</table>

(Continued)
TABLE 3.3 (Continued)
Examples of Chemicals Produced from Bio-Sources

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene glycol</td>
<td>Also known as 1,2-propanediol, propane-l,2-diol, and mono-propylene glycol; a viscous, colorless, odorless liquid that is nonvolatile at room temperature and is completely soluble in water; used in the production of consumer products such as antiperspirants, suntan lotions, eye drops, food flavorings, and bulking agent in oral, and topical drugs; industrial grade propylene glycol is used in the production of unsaturated polyester resins for end use markets such as residential and commercial construction, marine vessels, passenger vehicles, and consumer appliances; also used as an engine coolant and antifreeze in place of ethylene glycol, and in the airline industry as an airplane and runway de-icing agent; serves as a solvent, enzyme stabilizer, clarifying agent, and diluent; can be produced by hydrogenolysis of glycerin over mixed-metal catalysts, or hydrocracking of sorbitol.</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>A dicarboxylic acid that can be produced from biomass and used as a precursor for the synthesis of high-value products derived from renewable resources, including commodity chemicals, polymers, surfactants, and solvents.</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>Used to produce both terephthalic acid and dimethyl terephthalate which are raw materials for the production of polyethylene terephthalate bottles; can be produced via the traditional biochemical fermentation process followed by upgrading, thermochemical pyrolysis routes, and hybrid thermochemical/biochemical strategies of catalytic upgrading of sugars.</td>
</tr>
</tbody>
</table>

three main approaches: (i) purposeful cultivation of so-called clergy crops, (ii) harvesting natural vegetation, and (iii) collection of agricultural wastes. Thus, in the context of this book, biomass refers to (i) energy crops grown specifically to be used as fuel, such as fast-growing trees or switch grass; (ii) agricultural residues and byproducts, such as straw, sugarcane fiber, and rice hulls; and (iii) residues from forestry, construction, and other wood-processing industries (Detroyn, 1981; Vasudevan et al., 2005; Wright et al., 2006; Speight, 2008). It is the term used to describe any material of recent biological origin, including plant materials such as trees, grasses, agricultural crops, and even animal manure that can be converted to a variety of feedstocks for the production of petrochemical products through primary and/or secondary conversion methods (Table 3.4).

Biomass is a renewable energy source, unlike the fossil fuel resources (natural gas, crude oil, and coal) but, like the fossil fuels, biomass is a form of stored solar energy (Speight, 2008). The energy of the sun is captured through the process of photosynthesis in growing plants. One advantage of biofuel in comparison to most other fuel types is that it is biodegradable, and thus relatively harmless to the environment if spilled.

TABLE 3.4
Methods for the Conversion of Biomass to Petrochemical Feedstocks

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Conversion Type</th>
<th>Primary Method</th>
<th>Product</th>
<th>Secondary Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>Biological conversion</td>
<td>Fermentation</td>
<td>Methane</td>
<td>Gasification</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sugar</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pyrolysis</td>
<td>Protein</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrocarboxylation</td>
<td>Gas</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oil</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Char</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Gas</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Oil coke</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In order to produce fuels and chemicals, several currently available processes rely on entirely breaking down complex molecules before building up the desired compounds, such as the case with syngas production, to form alkanes and alcohols. While biomass can also be converted into syngas, an alternative and complimentary approach strategically converts biomass into chemical building blocks that retain features (e.g., electrophilic or nucleophilic character) that can be exploited in further manipulations. Such platform chemicals can be generated through either chemical routes or biological processes.

A major issue in the use of biomass is one of feedstock diversity. Biomass-based feedstock materials used in producing chemicals can be obtained from a large variety of sources. If considered individually, the number of potential renewable feedstocks can be overwhelming, but they tend to fall into three simple categories: (i) waste materials such as food processing wastes, (ii) dedicated feedstock crops which includes and short rotation woody crops or herbaceous energy crops such as perennials or forage crops and (iii) conventional food crops such as corn and wheat. In addition, these raw materials are composed of several similar chemical constituents, i.e., carbohydrates, proteins, lipids, lignin, and minerals.

Thermal or chemical processing of these materials is typically accomplished by novel separation and conversion methodology leading to chemicals similar to those from conventional petrochemical starting materials. Bioprocesses focus on microbiological conversion of fermentable sugars that are derived from these materials by thermal, chemical, or enzymatic means to commodity and specialty chemicals (Detroy, 1981). Thus, in choosing a feedstock for a given product, it is important not to be diverted by semantic differences that arise due to its current usage.

Biomass components, which are generally present in minor amounts, include triglycerides, sterols, alkaloids, resins, terpenes, terpenoids, and waxes. This includes everything from primary sources of crops and residues harvested/collected directly from the land to secondary sources such as sawmill residuals to tertiary sources of postconsumer residuals that often end up in landfills. A fourth source, although not usually categorized as such, includes the gases that result from anaerobic digestion of animal manure or organic waste in landfills (Wright et al., 2006; Speight, 2008).

Most present day production and use of biomass for energy is carried out in a very unsustainable manner with a great many negative environmental consequences. If biomass is to supply a greater proportion of the world’s energy needs in the future, the challenge will be to produce biomass and to convert and use it without harming the natural environment. Technologies and processes exist today which, if used properly, make biomass-based fuels less harmful to the environment than fossil fuels. Applying these technologies and processes on a site-specific basis in order to minimize negative environmental impacts is a prerequisite for sustainable use of biomass energy in the future. These technologies have the ability to be coordinated in a biorefinery.

A biorefinery (Speight, 2011c) is the means by which biomass can be converted to other products—in the current context the other products are biofuels which have the potential to replace certain petroleum-derived fuels. In theory, a biorefinery can use all kinds of biomass, including wood and dedicated agricultural crops, plant- and animal-derived waste, municipal waste, and aquatic biomass (algae, seaweeds). A biorefinery produces a spectrum of marketable products and energy including intermediate and final products: food, feed, materials, chemicals, fuels, power, and/or heat. However, the differences in the various biomass feedstocks may dictate that a biorefinery be constructed and operated on the basis of the chemical composition of the feedstock and the mean by which the feedstock is to be processed.

### 3.4.1 Biomass Feedstocks

More generally, biomass feedstocks are recognized or classified by the specific plant content of the feedstock or the manner in which the feedstocks is produced.

For example, primary biomass feedstocks are thus primary biomass that is harvested or collected from the field or forest where it is grown. Examples of primary biomass feedstocks currently being
used for bioenergy include grains and oilseed crops used for transportation fuel production, plus some crop residues (such as orchard trimmings and nut hulls) and some residues from logging and forest operations that are currently used for heat and power production.

**Secondary biomass feedstocks** differ from **primary biomass feedstocks** in that the secondary feedstocks are a byproduct of processing of the primary feedstocks. By *processing*, it is meant that there is substantial physical or chemical breakdown of the primary biomass and production of byproducts; *processors* may be factories or animals. Field processes such as harvesting, bundling, chipping, or pressing do not cause a biomass resource that was produced by photosynthesis (e.g., tree tops and limbs) to be classified as secondary biomass. **Specific examples of secondary biomass includes sawdust from sawmills, black liquor (which is a byproduct of paper making), and cheese whey (which is a byproduct of cheese-making processes). Manures from concentrated animal feeding operations are collectable secondary biomass resources. Vegetable oils used for biodiesel that are derived directly from the processing of oilseeds for various uses are also a secondary biomass resource.**

**Tertiary biomass feedstock** includes postconsumer residues and wastes, such as fats, greases, oils, construction and demolition wood debris, other waste wood from the urban environments, as well as packaging wastes, municipal solid wastes, and landfill gases. A category **other wood waste from the urban environment** includes trimmings from urban trees, which technically fits the definition of primary biomass. However, because this material is normally handled as a waste stream along with other postconsumer wastes from urban environments (and included in those statistics), it makes the most sense to consider it to be part of the tertiary biomass stream.

**Tertiary biomass** often includes fats and greases, which are byproducts of the reduction of animal biomass into component parts, since most fats and greases, and some oils, are not available for bioenergy use until after they become a postconsumer waste stream. Vegetable oils derived from processing of plant components and used directly for bioenergy (e.g., soybean oil used in biodiesel) would be a secondary biomass resource, though amounts being used for bioenergy are most likely to be tracked together with fats, greases, and waste oils.

One aspect of designing a refinery for any feedstocks is the composition of the feedstocks. For example, a heavy oil refinery would differ somewhat from a conventional refinery and a refinery for tar sand bitumen would be significantly different to both (Speight, 2008, 2014, 2017). Furthermore, the composition of biomass is variable (Speight, 2008) which is reflected in the range of heat value (heat content, calorific value) of biomass, which is somewhat lesser than for coal and much lower than the heat value for petroleum, generally falling in the range 6,000–8,500 Btu/lb (Speight, 2008). Moisture content is probably the most important determinant of heating value. Air-dried biomass typically has about 15%–20% moisture, whereas the moisture content for oven-dried biomass is around 0%. Moisture content is also an important characteristic of coals, varying in the range of 2%–30%. However, the bulk density (and hence energy density) of most biomass feedstocks is generally low, even after densification, about 10% and 40% of the bulk density of most fossil fuels.

The production of fuels and chemicals from renewable plant-based feedstocks utilizing state-of-the-art conversion technologies presents an opportunity to maintain competitive advantage and contribute to the attainment of national environmental targets. Bioprocessing routes have a number of compelling advantages over conventional petrochemicals production; however, it is only in the last decade that rapid progress in biotechnology has facilitated the commercialization of a number of plant-based chemical processes.

Plants offer a unique and diverse feedstock for chemicals and the production of biofuels from biomass requires some knowledge of the chemistry of biomass, the chemistry of the individual constituents of biomass, and the chemical means by which the biomass can be converted to fuel. It is widely recognized that further significant production of plant-based chemicals will only be economically viable in highly integrated and efficient production complexes producing a diverse range of chemical products. This biorefinery concept is analogous to conventional oil refineries and
petrochemical complexes that have evolved over many years to maximize process synergies, energy integration, and feedstock utilization to drive down production costs.

In addition, the specific components of plants such as carbohydrates, vegetable oils, plant fiber, and complex organic molecules known as primary and secondary metabolites can be utilized to produce a range of valuable monomers, chemical intermediates, pharmaceuticals, and materials.

### 3.4.1.1 Carbohydrates

Plants capture solar energy as fixed carbon during which carbon dioxide is converted to water and sugars $(\text{CH}_2\text{O})_x$:

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O})_x + \text{O}_2.$$  

The sugars produced are stored in three types of polymeric macromolecules: (i) starch, (ii) cellulose, and (iii) hemicellulose.

In general sugar polymers such as cellulose and starch can be readily broken down to their constituent monomers by hydrolysis, preparatory to conversion to ethanol or other chemicals (Vasudevan et al., 2005; Speight, 2008). In contrast, lignin is an unknown complex structure containing aromatic groups that is totally hypothetical and is less readily degraded than starch or cellulose. Although lignocellulose is one of the cheapest and most abundant forms of biomass, it is difficult to convert this relatively unreactive material into sugars. Among other factors, the walls of lignocellulose are composed of lignin, which must be broken down in order to render the cellulose and hemicellulose accessible to acid hydrolysis. For this reason, many efforts focused on ethanol production from biomass are based almost entirely on the fermentation of sugars derived from the starch in corn grain.

Carbohydrates (starch, cellulose, sugars): starch readily obtained from wheat and potato, while cellulose is obtained from wood pulp. The structures of these polysaccharides can be readily manipulated to produce a range of biodegradable polymers with properties similar to those of conventional plastics such as polystyrene foams and polyethylene film. In addition, these polysaccharides can be hydrolyzed, catalytically or enzymatically to produce sugars, a valuable fermentation feedstock for the production of ethanol, citric acid, lactic acid, and dibasic acids such as succinic acid.

### 3.4.1.2 Vegetable Oils

Vegetable oil is obtained from seed oil plants such as palm, sunflower, and soya. The predominant source of vegetable oils in many countries is rapeseed oil. Vegetable oils are a major feedstock for the oleo-chemicals industry (surfactants, dispersants, and personal care products) and are now successfully entering new markets such as diesel fuel, lubricants, polyurethane monomers, functional polymer additives, and solvents.

In many cases, it has been advocated that vegetable oil, and similar feedstocks, be used as feedstocks for a catalytic cracking unit. The properties of the product(s) can be controlled by controlling the process variables including the cracking temperature as well as the type of catalyst used. The production of biodiesel by direct esterification of fatty acids with short chain alcohols occurs in one step only whereby acidic catalysts can be used to speed up the reaction (Demirbaş, 2006).

### 3.4.1.3 Plant Fibers

Lignocellulosic fibers extracted from plants such as hemp and flax can replace cotton and polyester fibers in textile materials and glass fibers in insulation products. Lignin is a complex chemical that is most commonly derived from wood and is an integral part of the cell wall of plants. The chemical structure of lignin is unknown and, at best, can only be represented by hypothetical formulas.

Lignin (Latin: *lignum*—wood) is one of most abundant organic chemicals on earth after cellulose and chitin. By way of clarification, chitin $[(\text{C}_8\text{H}_{13}\text{O}_5\text{N})_n]$ is a long-chain polymeric polysaccharide of $\beta$-glucose that forms a hard, semitransparent material found throughout the natural world. Chitin is
the main component of the cell walls of fungi and is also a major component of the exoskeletons of arthropods, such as the crustaceans (e.g., crab, lobster, and shrimp), and insects (e.g., ants, beetles, and butterflies), and the beaks of cephalopods (e.g., squids and octopuses).

Lignin makes up about one-quarter to one-third of the dry mass of wood and is generally considered to be a large, cross-linked hydrophobic, aromatic macromolecules with a molecular mass that is estimated to be in excess of 10,000. Lignin fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components and is covalently linked (bonded) to hemicellulose. Lignin also forms covalent bonds with polysaccharides which enables cross-linking to different plant polysaccharides. Lignin confers mechanical strength to the cell wall (stabilizing the mature cell wall) and therefore the entire plant.

3.4.2 Biorefining

A petroleum refinery is a series of integrated unit processes by which petroleum can be converted to a slate of useful (salable) products. A petroleum refinery, as currently configured is unsuitable for processing raw, or even partially processed, biomass. A typical refinery might be suitable for processing products such as gases, liquid, or solids products from biomass processing. These products from biomass might be acceptable as a single feedstock to a specific unit or, more likely, as a feedstock to be blended with refinery streams to be coprocessed in various refinery units.

Thus, a biorefinery might, in the early stages of development, be a series of unit processes which convert biomass to a primary product that requires further processing to become the final salable product. The analogy is in the processing of bitumen from tar sand which is first processed to a synthetic crude oil (primary processing) and then sent to a refinery for conversion to salable fuel products (Speight, 2008, 2014, 2017).

Analogous, in many cases, to the thermal decomposition of crude oil constituents, in the flash pyrolysis (high-temperature cracking and short residence time), the products are ethylene, benzene, toluene, and the xylene isomers as well as carbon monoxide and carbon dioxide. The type of biomass (for example, wood) used influences the product distribution (Steinberg et al., 1992). Theoretically, the flash pyrolysis process can use a wide range of biomass sources. The process has much in common with the naphtha cracking process.

At this point in the context of flash pyrolysis, it is worthy of note that plastic waste (while not a biomass material) can also be treated by flash pyrolysis to produce starting materials for petrochemical manufacture. In the process, the mixed plastic waste is heated in an oxygen-free atmosphere. At a temperature of several hundred degrees, the constituents of the waste decompose to yield a mixture of gaseous, liquid, and solids. The composition of the product depends on temperature and pressure—the higher the temperature, the more gaseous products are formed. An important fraction of this gaseous product is ethylene if plastics are used as feedstock.

Biorefining in which biomass is converted into a variety of chemical products is not new if activities such as production of vegetable oils, beer, and wine requiring pretreatment are considered. Many of these activities are known to have been in practice for millennia. Biomass can be converted into commercial fuels, suitable to substitute for fossil fuels. These can be used for transportation, heating, electricity generation or anything else fossil fuels are used for. The conversion is accomplished through the use of several distinct processes which include both biochemical conversion and thermal conversion to produce gaseous, liquid, and solid fuels which have high energy contents, are easily transportable, and are therefore suitable for use as commercial fuels.

Biorefining offers a method to accessing the integrated production of chemicals, materials, and fuels. Although the concept of a biorefinery concept is analogous to that of an oil refinery, the differences in the various biomass feedstocks require a divergence in the methods used to convert the feedstocks to fuels and chemicals (Speight, 2014, 2017). Thus, a biorefinery, like a petroleum refinery, may need to be a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. In a manner similar to the petroleum refinery,
a biorefinery would integrate a variety of conversion processes to produce multiple product streams such as motor fuels and other chemicals from biomass such as the inclusion of gasification processes and fermentation processes to name only two possible processes options.

In short, a biorefinery should combine the essential technologies to transform biological raw materials into a range of industrially useful intermediates. However, the type of biorefinery would have to be differentiated by the character of the feedstock. For example, the crop biorefinery would use raw materials such as cereals or maize and the lignocellulose biorefinery would use raw material with high cellulose content, such as straw, wood, and paper waste.

As a petroleum refinery uses petroleum as the major input and processes it into many different products, a biorefinery with feedstocks such as lignocellulosic biomass as the major input and would processes it into many different products. Currently, wet-mill corn processing and pulp and paper mills can be categorized into biorefineries since they produce multiple products from biomass. Research is currently being conducted to foster new industries to convert biomass into a wide range of products, including ones that would otherwise be made from petrochemicals. The idea is for biorefineries to produce both high-volume liquid fuels and high-value chemicals or products in order to address national energy needs while enhancing operation economics.

However, the different compositional nature of the biomass feedstock, compared to crude oil, will require the application of a wider variety of processing tools in the biorefinery. Processing the individual components will utilize conventional thermochemical operations and state-of-the-art bioprocessing techniques. Although a number of new bioprocesses have been commercialized, it is clear that economic and technical barriers still exist before the full potential of this area can be realized. The biorefinery concept could significantly reduce production costs of plant-based chemicals and facilitate their substitution into existing markets. This concept is analogous to that of a modern oil refinery in that the biorefinery is a highly integrated complex that will efficiently separate biomass raw materials into individual components and convert these into marketable products such as energy, fuels, and chemicals. By analogy with crude oil, every element of the plant feedstock will be utilized including the low-value lignin components.

A key requirement for the biorefinery is the ability of the refinery to develop process technology that can economically access and convert the five- and six-membered ring sugars present in the cellulose and hemicellulose fractions of the lignocellulosic feedstock. Although engineering technology exists to effectively separate the sugar-containing fractions from the lignocellulose, the enzyme technology to economically convert the five ring sugars to useful products requires further development.

Plants are very effective chemical mini-factories or refineries insofar as they produce chemicals by specific pathways. The chemicals they produce are usually essential manufactures (called metabolites) including sugars and amino acids that are essential for the growth of the plant, as well as more complex compounds. Unlike petroleum-derived in petrochemicals where most chemicals are built from the bottom-up, bio-feedstocks already have some valuable products to skim off the top before being broken down and used to build new molecules.

As a feedstock, biomass can be converted by thermal or biological routes to a wide range of useful forms of energy including process heat, steam, electricity, as well as liquid fuels, chemicals, and synthesis gas. As a raw material, biomass is a nearly universal feedstock due to its versatility, domestic availability, and renewable character. At the same time, it also has its limitations. For example, the energy density of biomass is low compared to that of coal, liquid petroleum, or petroleum-derived fuels. The heat content of biomass, on a dry basis (7,000–9,000 Btu/lb) is at best comparable with that of a low-rank coal or lignite, and substantially (50%–100%) lower than that of anthracite, most bituminous coals, and petroleum. Most biomass, as received, has a high burden of physically adsorbed moisture, up to 50% by weight. Thus, without substantial drying, the energy content of a biomass feed per unit mass is even less. These inherent characteristics and limitations of biomass feedstocks have focused the development of efficient methods of chemically transforming and upgrading biomass feedstocks in a refinery.
The sugar-base involves breakdown of biomass into raw component sugars using chemical and biological means. The raw fuels may then be upgraded to produce fuels and chemicals that are interchangeable with existing commodities such as transportation fuels, oils, and hydrogen.

Although a number of new bioprocesses have been commercialized, it is clear that economic and technical barriers still exist before the full potential of this area can be realized. One concept gaining considerable momentum is the biorefinery which could significantly reduce production costs of plant-based chemicals and facilitate their substitution into existing markets. This concept is analogous to that of a modern oil refinery in that the biorefinery is a highly integrated complex that will efficiently separate biomass raw materials into individual components and convert these into marketable products such as energy, fuels, and chemicals.

By analogy with crude oil; every element of the plant feedstock will be utilized including the low-value lignin components. However, the different compositional nature of the biomass feedstock, compared to crude oil, will require the application of a wider variety of processing tools in the biorefinery. Processing of the individual components will utilize conventional thermochemical operations and state-of-the-art bioprocessing techniques. The production of biofuels in the biorefinery complex will service existing high-volume markets, providing economy-of-scale benefits and large volumes of byproduct streams at minimal cost for upgrading to valuable chemicals. A pertinent example of this is the production of glycerol (glycerin) as a byproduct in biodiesel plants.

Glycerol has high functionality and is a potential platform chemical for conversion into a range of higher-value chemicals. The high-volume product streams in a biorefinery need not necessarily be a fuel but could also be a large-volume chemical intermediate such as ethylene or lactic acid. In addition to a variety of methods techniques can be employed to obtain different product portfolios of bulk chemicals, fuels, and materials. Biotechnology-based conversion processes can be used to ferment the biomass carbohydrate content into sugars that can then be further processed. As one example, the fermentation path to lactic acid shows promise as a route to biodegradable plastics. An alternative is to employ thermochemical conversion processes which use pyrolysis or gasification of biomass to produce a hydrogen-rich synthesis gas which can be used in a wide range of chemical processes.

A key requirement for delivery of the biorefinery is the ability of the refinery to develop and use process technology that can economically access and convert the five- and six-membered ring sugars present in the cellulose and hemicellulose fractions of the lignocellulosic feedstock. Although engineering technology exists to effectively separate the sugar-containing fractions from the lignocellulose, the enzyme technology to economically convert the five ring sugars to useful products requires further development.

The construction of both large biofuel and renewable chemical production facilities coupled with the pace at which bioscience is being both developed and applied demonstrates that the utilization of nonfood crops will become more significant in the near term. The biorefinery concept provides a means to significantly reduce production costs such that a substantial substitution of petrochemicals by renewable chemicals becomes possible. However, significant technical challenges remain before the biorefinery concept can be realized.

If the biorefinery is truly analogous to an oil refinery in which crude oil is separated into a series of products, such as gasoline, heating oil, jet fuel, and petrochemicals, the biorefinery can take advantage of the differences in biomass components and intermediates and maximize the value derived from the biomass feedstock. A biorefinery might, for example, produce one or several low-volume, but high-value, chemical products and a low-value, but high-volume liquid transportation fuel, while generating electricity and process heat for its own use and perhaps enough for sale of electricity. The high-value products enhance profitability, the high-volume fuel helps meet national energy needs, and the power production reduces costs and avoids greenhouse gas emissions.

The basic types of processes used to generate chemicals from biomass as might be incorporated into a biorefinery are: (i) pyrolysis, (ii) gasification, (iii) anaerobic digestion, and (iv) fermentation.
3.4.2.1 Pyrolysis

Pyrolysis is a medium temperature method which produces gas, oil, and char from crops which can then be further processed into useful fuels or feedstock (Boateng et al., 2007). Pyrolysis is the direct thermochemical conversion processes which include pyrolysis, liquefaction, and solvolysis (Kavalov and Peteves, 2005).

Wood and many other similar types of biomass which contain lignin and cellulose (such as agricultural wastes, cotton gin waste, wood wastes, and peanut hulls) can be converted through a thermochemical process, such as pyrolysis, into solid, liquid, or gaseous fuels. Pyrolysis, used to produce charcoal since the dawn of civilization, is still the most common thermochemical conversion of biomass to commercial fuel.

During pyrolysis, biomass is heated in the absence of air and breaks down into a complex mixture of liquids, gases, and a residual char. If wood is used as the feedstock, the residual char is what is commonly known as charcoal. With more modern technologies, pyrolysis can be carried out under a variety of conditions to capture all the components, and to maximize the output of the desired product be it char, liquid, or gas. Pyrolysis is often considered to be the gasification of biomass in the absence of oxygen. However, the chemistry of each process may differ significantly. In general, biomass does not gasify as easily as coal, and it produces other hydrocarbon compounds in the gas mixture exiting the gasifier; this is especially true when no oxygen is used. As a result, typically an extra step must be taken to reform these hydrocarbon derivatives with a catalyst to yield a clean syngas mixture of hydrogen, carbon monoxide, and carbon dioxide.

Fast pyrolysis is a thermal decomposition process that occurs at moderate temperatures with a high heat transfer rate to the biomass particles and a short hot vapor residence time in the reaction zone. Several reactor configurations have been shown to assure this condition and to achieve yields of liquid product as high as 75% based on the starting dry biomass weight. They include bubbling fluid beds, circulating and transported beds, cyclonic reactors, and ablative reactors.

Fast pyrolysis of biomass produces a liquid product, pyrolysis oil or bio-oil that can be readily stored and transported. Pyrolysis oil is a renewable liquid fuel and can also be used for production of chemicals. Fast pyrolysis has now achieved a commercial success for production of chemicals and is being actively developed for producing liquid fuels. Pyrolysis oil has been successfully tested in engines, turbines, and boilers, and been upgraded to high-quality hydrocarbon fuels. In the 1990s, several fast pyrolysis technologies reached near-commercial status and the yields and properties of the generated liquid product, bio-oil, depend on the feedstock, the process type and conditions, and the product collection efficiency.

Direct hydrothermal liquefaction involves converting biomass to an oily liquid by contacting the biomass with water at elevated temperatures (300°C–350°C, 570°F–660°F) with sufficient pressure to maintain the water primarily in the liquid phase for residence times up to 30 min. Alkali may be added to promote organic conversion. The primary product is an organic liquid with reduced oxygen content (about 10%) and the primary byproduct is water containing soluble organic compounds.

The importance of the provisions for the supply of feedstocks as crops and other biomass are often underestimated since it is assumed that the supplies are inexhaustible. While this may be true over the long term, short-term supply of feedstocks can be as much as risk as any venture.

3.4.2.2 Gasification

Alternatively, biomass can be converted into fuels and chemicals indirectly (by gasification to syngas followed by catalytic conversion to liquid fuels) (Molino et al., 2016). Biomass gasification is a mature technology pathway that uses a controlled process involving heat, steam, and oxygen to convert biomass to hydrogen and other products, without combustion and represents an efficient process for the production of chemicals and hydrogen.

Gasification is a process that converts organic carbonaceous feedstocks into carbon monoxide, carbon dioxide, and hydrogen by reacting the feedstock at high temperatures (>700°C, 1,290°F),
without combustion, with a controlled amount of oxygen and/or steam. The resulting gas mixture (synthesis gas, syngas, or producer gas) is itself a fuel. The power derived from carbonaceous feedstocks and gasification followed by the combustion of the product gas(es) is considered to be a source of renewable energy if the gaseous products are from a source (e.g., biomass) other than a fossil fuel. The carbon monoxide can then be reacted with water (steam) to form carbon dioxide and more hydrogen via a water-gas shift reaction. Adsorber or special membranes can separate the hydrogen from this gas stream. The simplified reaction is:

\[
C_6H_{12}O_6 + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + \text{other species}
\]

\[
CO + H_2O \rightarrow CO_2 + H_2 \text{(water-gas shift reaction)}
\]

This reaction scheme uses glucose as a surrogate for cellulose but it must be recognized that biomass has highly variable composition and complexity with cellulose as one major component.

Coal has, for many decades, been the primary feedstock for gasification units—coal can also be gasified in situ (in the underground seam) (Speight, 2013a), but that is not the subject of this text and is not discussed further. However, with the concern on the issue of environmental pollutants and the potential shortage of coal in some areas there is a move to feedstocks other than coal for gasification processes. Gasification permits the utilization of various feedstocks (coal, biomass, petroleum resids, and other carbonaceous wastes) to their fullest potential.

The advantage of the gasification process when a carbonaceous feedstock (a feedstock containing carbon) or hydrocarbonaceous feedstock (a feedstock containing carbon and hydrogen) is employed is that the product of focus—synthesis gas—is potentially more useful as an energy source and results in an overall cleaner process. The production of synthesis gas is a more efficient production of an energy source than, say, the direct combustion of the original feedstock because synthesis gas can be converted via the Fischer–Tropsch process into a range of synthesis liquid fuels suitable for using gasoline engines or diesel engines (Chapter 10) (Chadeesingh, 2011).

Biomass includes a wide range of materials that produce a variety of products which are dependent upon the feedstock (Balat, 2011; Demirbaş, 2011; Ramroop Singh, 2011; Speight, 2011a). For example, typical biomass wastes include wood material (bark, chips, scraps, and saw dust), pulp and paper industry residues, agricultural residues, organic municipal material, sewage, manure, and food processing byproducts. Agricultural residues such as straws, nut shells, fruit shells, fruit seeds, plant stalks and stover, green leaves, and molasses are potential renewable energy resources. Many developing countries have a wide variety of agricultural residues in ample quantities. Large quantities of agricultural plant residues are produced annually worldwide and are vastly underutilized. Agricultural residues, when used as fuel, through direct combustion, only a small percentage of their potential energy is available, due to inefficient burners used. Current disposal methods for these agricultural residues have caused widespread environmental concerns. For example, disposal of rice and wheat straw by open-field burning causes air pollution. In addition, the widely varying heat content of the different types of biomass varies widely and must be taken into consideration when designing any conversion process (Jenkins and Ebeling, 1985).

Raw materials that can be used to produce biomass fuels are widely available and arise from a large number of different sources and in numerous forms. Biomass can also be used to produce electricity—either blended with traditional feedstocks, such as coal or by itself. However, each of the biomass materials can be used to produce fuel but not all forms are suitable for all the different types of energy conversion technologies such as biomass gasification (Rajvanshi, 1986; Brigwater, 2003; Dasappa et al., 2004; Speight, 2011a; Basu, 2013). The main basic sources of biomass material are: (i) wood, including bark, logs, sawdust, wood chips, wood pellets and briquettes, (ii) high yield energy crops, such as wheat, that are grown specifically for energy applications, (iii) agricultural crop and animal residues, like straw or slurry, (iv) food waste, both domestic and commercial, and (v) industrial waste, such as wood pulp or paper pulp. For processing, a simple form of biomass such
as untreated and unfinished wood may be cut into a number of physical forms, including pellets and wood chips, for use in biomass boilers and stoves.

Thermal conversion processes use heat as the dominant mechanism to convert biomass into another chemical form. The basic alternatives of combustion, torrefaction, pyrolysis, and gasification are separated principally by the extent to which the chemical reactions involved are allowed to proceed (mainly controlled by the availability of oxygen and conversion temperature) (Speight, 2011a).

Many forms of biomass contain a high percentage of moisture (along with carbohydrates and sugars) and mineral constituents—both of which can influence the viability of a gasification process (Chapter 3)—the presence of high levels of moisture in the biomass reduces the temperature inside the gasifier, which then reduces the efficiency of the gasifier. Therefore, many biomass gasification technologies require that the biomass be dried to reduce the moisture content prior to feeding into the gasifier. In addition, biomass can come in a range of sizes. In many biomass gasification systems, the biomass must be processed to a uniform size or shape to feed into the gasifier at a consistent rate and to ensure that as much of the biomass is gasified as possible.

Biomass, such as wood pellets, yard and crop wastes, and the so-called energy crops such as switch grass and waste from pulp and paper mills can be used to produce ethanol and synthetic diesel fuel. The biomass is first gasified to produce the synthetic gas (synthesis gas), and then converted via catalytic processes to these downstream products. Furthermore, most biomass gasification systems use air instead of oxygen for the gasification reactions (which is typically used in large-scale industrial and power gasification plants). Gasifiers that use oxygen require an air separation unit to provide the gaseous/liquid oxygen; this is usually not cost-effective at the smaller scales used in biomass gasification plants. Air-blown gasifiers use the oxygen in the air for the gasification reactions.

In general, biomass gasification plants are much smaller than the typical coal or petroleum coke gasification plants used in the power, chemical, fertilizer, and refining industries—the sustainability of the fuel supply is often brought into question. As such, a biomass gasification plant is less expensive to construct and has a smaller environmental footprint. For example, while a large industrial gasification plant may take up to 150 acres of land and process 2,500–15,000 tons per day of feedstock (such as coal or petroleum coke), the smaller biomass plants typically process 25–200 tons of feedstock per day and take up less than 10 acres.

Biomass gasification has been the focus of research in recent years to estimate efficiency and performance of the gasification process using various types of biomass such as sugarcane residue (Gabra et al., 2001), rice hulls (Boateng et al., 1992), pine sawdust (Lv et al., 2004), almond shells (Rapagnà and Latif, 1997; Rapagnà et al., 2000), wheat straw (Ergudenler and Ghaly, 1993), food waste (Ko et al., 2001), and wood biomass (Pakdel and Roy, 1991; Bhattacharya et al., 1999; Chen et al., 1992; Hanaoka et al., 2005). Recently, co-gasification of various biomass and coal mixtures has attracted a great deal of interest from the scientific community. Feedstock combinations including Japanese cedar wood and coal (Kumabe et al., 2007), coal and saw dust, coal and pine chips (Pan et al., 2000), coal and silver birch wood (Collot et al., 1999), and coal and birch wood (Brage et al., 2000) have been reported in gasification practice. Co-gasification of coal and biomass has some synergy—the process not only produces a low carbon footprint on the environment, but also improves the \(\text{H}_2/\text{CO}\) ratio in the produced gas which is required for liquid fuel synthesis (Sjöström et al., 1999; Kumabe et al., 2007). In addition, the inorganic matter present in biomass catalyzes the gasification of coal. However, co-gasification processes require custom fittings and optimized processes for the coal and region-specific wood residues.

While co-gasification of coal and biomass is advantageous from a chemical viewpoint, some practical problems are present on upstream, gasification, and downstream processes. On the upstream side, the particle size of the coal and biomass is required to be uniform for optimum gasification. In addition, moisture content and pretreatment (torrefaction) are very important during upstream processing.
While upstream processing is influential from a material handling point of view, the choice of gasifier operation parameters (temperature, gasifying agent, and catalysts) dictate the product gas composition and quality. Biomass decomposition occurs at a lower temperature than coal and therefore different reactors compatible to the feedstock mixture are required (Speight, 2011c; Brar et al., 2012; Speight, 2013a, 2013b). Furthermore, feedstock and gasifier type along with operating parameters not only decide product gas composition but also dictate the amount of impurities to be handled downstream.

Downstream processes need to be modified if coal is co-gasified with biomass. Heavy metal and impurities such as sulfur and mercury present in coal can make synthesis gas difficult to use and unhealthy for the environment. Alkali present in biomass can also cause corrosion problems high temperatures in downstream pipes. An alternative option to downstream gas cleaning would be to process coal to remove mercury and sulfur prior to feeding into the gasifier.

However, first and foremost, coal and biomass require drying and size reduction before they can be fed into a gasifier. Size reduction is needed to obtain appropriate particle sizes; however, drying is required to achieve moisture content suitable for gasification operations. In addition, biomass densification may be conducted to prepare pellets and improve density and material flow in the feeder areas.

It is recommended that biomass moisture content should be less than 15% w/w prior to gasification. High moisture content reduces the temperature achieved in the gasification zone, thus resulting in incomplete gasification. Forest residues or wood has a fiber saturation point at 30%–31% moisture content (dry basis) (Brar et al., 2012). Compressive and shear strength of the wood increases with decreased moisture content below the fiber saturation point. In such a situation, water is removed from the cell wall leading to shrinkage. The long-chain molecule constituents of the cell wall move closer to each other and bind more tightly. A high level of moisture, usually injected in form of steam in the gasification zone, favors formation of a water-gas shift reaction that increases hydrogen concentration in the resulting gas.

The torrefaction process is a thermal treatment of biomass in the absence of oxygen, usually at 250°C–300°C (480°F–570°F) to drive off moisture, decompose hemicellulose completely, and partially decompose cellulose (Speight, 2011a). Torrefied biomass has reactive and unstable cellulose molecules with broken hydrogen bonds and not only retains 79%–95% of feedstock energy but also produces a more reactive feedstock with lower atomic hydrogen-carbon and oxygen-carbon ratios to those of the original biomass. Torrefaction results in higher yields of hydrogen and carbon monoxide in the gasification process.

Most small- to medium-sized biomass/waste gasifiers are air blown, operated at atmospheric pressure, and at temperatures in the range 800°C–100°C (1,470°F–2,190°F). They face very different challenges compared to large gasification plants—the use of a small-scale air separation plant should oxygen gasification be preferred. Pressurized operation, which eases gas cleaning, may not be practical.

Biomass fuel producers, coal producers, and, to a lesser extent, waste companies are enthusiastic about supplying co-gasification power plants and realize the benefits of co-gasification with alternate fuels (Speight, 2008, 2011a; Lee and Shah, 2013; Speight, 2013a, 2013b). The benefits of a co-gasification technology involving coal and biomass include the use of a reliable coal supply with gate fee waste and biomass that allows the economies of scale from a larger plant to be supplied just with waste and biomass. In addition, the technology offers a future option of hydrogen production and fuel development in refineries. In fact, oil refineries and petrochemical plants are opportunities for gasifiers when the hydrogen is particularly valuable (Speight, 2011b, 2014).

In addition, while biomass may seem to some observers to be the answer to the global climate change issue, the advantages and disadvantages must be considered carefully. For example, the advantages are (i) biomass is a theoretically inexhaustible fuel source, (ii) when direct conversion of combustion of plant mass—such as fermentation and pyrolysis—is not used to generate energy there is minimal environmental impact, (iii) alcohols and other fuels produced by biomass are efficient, viable, and relatively clean-burning, and (iv) biomass is available on a worldwide basis.
On the other hand, the disadvantages include (i) the highly variable heat content of different biomass feedstocks, (ii) the high water content that can affect the process energy balance, and (iii) there is a potential net loss of energy when a biomass plant is operated on a small scale—an account of the energy put used to grow and harvest the biomass must be included in the energy balance.

### 3.4.2.3 Anaerobic Digestion

*Anaerobic digestion* is a natural process and is the microbiological conversion of organic matter to methane in the absence of oxygen. The *biochemical conversion* of biomass is completed through alcoholic fermentation to produce liquid fuels and anaerobic digestion or fermentation, resulting in biogas (hydrogen, carbon dioxide, ammonia, and methane) usually through four steps (hydrolysis, acidogenesis, acetogenesis, and methanogenesis):

#### Hydrolysis:

- Carbohydrates → sugars
- Fats → fatty acids
- Proteins → amino acids

#### Acidogenesis:

- Sugars → carbon acids + alcohols + hydrogen + carbon dioxide + ammonia
- Fatty acids → carbon acids + alcohols + hydrogen, carbon dioxide + ammonia
- Amino acids → carbon acids + alcohols + hydrogen, carbon dioxide + ammonia

#### Acetogenesis:

- Carbon acids + alcohols → acetic acid + carbon dioxide + hydrogen

#### Methanogenesis:

- Acetic acid → methane + carbon dioxide

The decomposition is caused by natural bacterial action in various stages and occurs in a variety of natural anaerobic environments, including water sediment, water-logged soils, natural hot springs, ocean thermal vents, and the stomach of various animals (e.g., cows). The digested organic matter resulting from the anaerobic digestion process is usually called *digestate*.

Symbiotic groups of bacteria perform different functions at different stages of the digestion process. There are four basic types of microorganisms involved (i) hydrolytic bacteria breakdown complex organic wastes into sugars and amino acids; (ii) fermentative bacteria then convert those products into organic acids; (iii) acidogenic microorganisms convert the acids into hydrogen, carbon dioxide, and acetate; and (iv) methanogenic bacteria produce biogas from acetic acid, hydrogen, and carbon dioxide.

The process of anaerobic digestion occurs in a sequence of stages involving distinct types of bacteria. Hydrolytic and fermentative bacteria first breakdown the carbohydrates, proteins, and fats present in biomass feedstock into fatty acids, alcohol, carbon dioxide, hydrogen, ammonia, and sulfides. This stage is called hydrolysis (or liquefaction). Next, acetogenic (acid-forming) bacteria further digest the products of hydrolysis into acetic acid, hydrogen, and carbon dioxide. Methanogenic (methane-forming) bacteria then convert these products into biogas.
The combustion of digester gas can supply useful energy in the form of hot air, hot water, or steam. After filtering and drying, digester gas is suitable as fuel for an internal combustion engine, which, combined with a generator, can produce electricity. Future applications of digester gas may include electric power production from gas turbines or fuel cells. Digester gas can substitute for natural gas or propane in space heaters, refrigeration equipment, cooking stoves, or other equipment. Compressed digester gas can be used as an alternative transportation fuel.

There are three principal byproducts of anaerobic digestion: (i) biogas, (ii) acidogenic digestate, and (iii) methanogenic digestate.

**Biogas** is a gaseous mixture comprising mostly methane and carbon dioxide, and also containing a small amount of hydrogen and occasionally trace levels of hydrogen sulfide. Since the gas is not released directly into the atmosphere and the carbon dioxide comes from an organic source with a short carbon cycle, biogas does not contribute to increasing atmospheric carbon dioxide concentrations; because of this, it is considered to be an environmentally friendly energy source. The production of biogas is not a steady stream; it is highest during the middle of the reaction. In the early stages of the reaction, little gas is produced because the number of bacteria is still small. Toward the end of the reaction, the hardest to digest materials remain, leading to a decrease in the amount of biogas produced.

The second byproduct (**acidogenic digestate**) is a stable organic material comprised largely of lignin and chitin and a variety of mineral components in a matrix of dead bacterial cells; some plastic may also be present. This resembles domestic compost and can be used as compost or to make low-grade building products such as fiberboard.

The third byproduct is a liquid (**methanogenic digestate**) that is rich in nutrients and can be an excellent fertilizer dependent on the quality of the material being digested. If the digested materials include low levels of toxic heavy metals or synthetic organic materials such as pesticides or polychlorobiphenyls, the effect of digestion is to significantly concentrate such materials in the digester liquor. In such cases, further treatment will be required in order to dispose of this liquid properly. In extreme cases, the disposal costs and the environmental risks posed by such materials can offset any environmental gains provided by the use of biogas. This is a significant risk when treating sewage from industrialized catchments.

Nearly all digestion plants have ancillary processes to treat and manage all the byproducts. The gas stream is dried and sometimes sweetened before storage and use. The sludge liquor mixture has to be separated by one of a variety of ways, the most common of which is filtration. Excess water is also sometimes treated in sequencing batch reactors for discharge into sewers or for irrigation. Digestion can be either **wet** or **dry**. Dry digestion refers to mixtures which have a solid content of 30% or greater, whereas wet digestion refers to mixtures of 15% or less.

In recent years, increasing awareness that anaerobic digesters can help control the disposal and odor of animal waste has stimulated renewed interest in the technology. New digesters now are being built because they effectively eliminate the environmental hazards of dairy farms and other animal feedlots. Anaerobic digester systems can reduce fecal coliform bacteria in manure by more than 99%, virtually eliminating a major source of water pollution. Separation of the solids during the digester process removes about 25% of the nutrients from manure, and the solids can be sold out of the drainage basin where nutrient loading may be a problem. In addition, the digester’s ability to produce and capture methane from the manure reduces the amount of methane that otherwise would enter the atmosphere. Scientists have targeted methane gas in the atmosphere as a contributor to global climate change.

Controlled anaerobic digestion requires an airtight chamber, called a digester. To promote bacterial activity, the digester must maintain a temperature of at least 68°F. Using higher temperatures, up to 150°F, shortens processing time and reduces the required volume of the tank by 25%–40%. However, there are more species of anaerobic bacteria that thrive in the temperature range of a standard design (mesophilic bacteria) than there are species that thrive at higher temperatures (thermophilic bacteria). High-temperature digesters also are more prone to upset
because of temperature fluctuations and their successful operation requires close monitoring and
diligent maintenance.

The biogas produced in a digester (digester gas) is actually a mixture of gases, with methane and
carbon dioxide making up more than 90% of the total. Biogas typically contains smaller amounts
of hydrogen sulfide, nitrogen, hydrogen, methyl mercaptans, and oxygen.

Methane is a combustible gas. The energy content of digester gas depends on the amount of
methane it contains. Methane content varies from about 55% to 80%. Typical digester gas, with
a methane concentration of 65%, contains about 600 Btu of energy per cubic foot. There are three
basic digester designs and all of them can trap methane and reduce fecal coliform bacteria, but
they differ in cost, climate suitability, and the concentration of manure solids they can digest: (i) a covered lagoon digester, (ii) a complete mix digester, (iii) a plug-flow digester.

A covered lagoon digester, as the name suggests, consists of a manure storage lagoon with a
cover. The cover traps gas produced during decomposition of the manure. This type of digester
is the least expensive of the three. Covering a manure storage lagoon is a simple form of digester
technology suitable for liquid manure with less than 3% solids. For this type of digester, an
impermeable floating cover of industrial fabric covers all or part of the lagoon. A concrete foot-
ing along the edge of the lagoon holds the cover in place with an airtight seal. Methane produced
in the lagoon collects under the cover. A suction pipe extracts the gas for use. Covered lagoon
digesters require large lagoon volumes and a warm climate. Covered lagoons have low capital
cost, but these systems are not suitable for locations in cooler climates or locations where a high
water table exists.

A complete mix digester converts organic waste to biogas in a heated tank above or below ground.
A mechanical or gas mixer keeps the solids in suspension. Complete mix digesters are expensive to
construct and cost more than plug-flow digesters to operate and maintain. Complete mix digesters
are suitable for larger manure volumes having solids concentration of 3%–10%. The reactor is a
round steel or poured concrete container. During the digestion process, the manure slurry is con-
tinuously mixed to keep the solids in suspension. Biogas accumulates at the top of the digester. The
biogas can be used as fuel for an engine-generator to produce electricity or as boiler fuel to produce
steam. Using waste heat from the engine or boiler to warm the slurry in the digester reduces reten-
tion time to less than 20 days.

A plug-flow digester is suitable for ruminant animal manure that has a solids concentration of
11%–13%. A typical design for a plug-flow system includes a manure collection system, a mixing
pit, and the digester itself. In the mixing pit, the addition of water adjusts the proportion of solids in
the manure slurry to the optimal consistency. The digester is a long, rectangular container, usually
built below-grade, with an airtight, expandable cover.

New material added to the tank at one end pushes older material to the opposite end. Coarse
solids in ruminant manure form a viscous material as they are digested, limiting solids separation in
the digester tank. As a result, the material flows through the tank in a plug. Average retention time
(the time a manure plug remains in the digester) is 20–30 days. Anaerobic digestion of the manure
slurry releases biogas as the material flows through the digester. A flexible, impermeable cover on
the digester traps the gas. Pipes beneath the cover carry the biogas from the digester to an engine-
generator set.

A plug-flow digester requires minimal maintenance. Waste heat from the engine-generator can
be used to heat the digester. Inside the digester, suspended heating pipes allow hot water to circu-
late. The hot water heats the digester to keep the slurry at 25°C–40°C (77°F–104°F), a temperature
range suitable for methane-producing bacteria. The hot water can come from recovered waste heat
from an engine-generator fueled with digester gas or from burning digester gas directly in a boiler.

Anaerobic digestion of biomass has been practiced for almost a century, and is very popular
in many developing countries such as China and India. The organic fraction of almost any form
of biomass, including sewage sludge, animal wastes, and industrial effluents, can be broken down
through anaerobic digestion into methane and carbon dioxide. This biogas is a reasonably clean
burning fuel that can be captured and put to many different end uses such as cooking, heating, or electrical generation.

### 3.4.2.4 Fermentation

A number of processes allow biomass to be transformed into gaseous fuels such as methane or hydrogen (Sørensen et al., 2006). One pathway uses algae and bacteria that have been genetically modified to produce hydrogen directly instead of the conventional biological energy carriers. A second pathway uses plant material such as agricultural residues in a fermentation process leading to biogas from which the desired fuels can be isolated. This technology is established and in widespread use for waste treatment, but often with the energy produced only for on-site use, which often implies less than maximum energy yields. Finally, high-temperature gasification supplies a crude gas, which may be transformed into hydrogen by a second reaction step. In addition to biogas, there is also the possibility of using the solid byproduct as a biofuel.

Traditional fermentation plants producing biogas are in routine use, ranging from farms to large municipal plants. As feedstock they use manure, agricultural residues, urban sewage and waste from households, and the output gas is typically 64% methane. The biomass conversion process is accomplished by a large number of different agents, from the microbes decomposing and hydrolyzing plant material, over the acidophilic bacteria dissolving the biomass in aquatic solution, and to the strictly anaerobic methane bacteria responsible for the gas formation. Operating a biogas plant for a period of some months usually makes the bacterial composition stabilize in a way suitable for obtaining high conversion efficiency (typically above 60%, the theoretical limit being near to 100%), and it is found important not to vary the feedstock compositions abruptly, if optimal operation is to be maintained. Operating temperatures for the bacterial processes are only slightly above ambient temperatures, e.g., in the mesophilic region around 30°C.

The production of ethanol from corn is a mature technology that holds much potential (Nichols et al., 2006). Substantial cost reductions may be possible, however, if cellulose-based feedstocks are used instead of corn. The feed for all ethanol fermentations is sugar—traditionally a hexose (a six-carbon or “C₆” sugar) such as those present naturally in sugar cane, sugar beet, and molasses. Sugar for fermentation can also be recovered from starch, which is actually a polymer of hexose sugars (polysaccharide).

Biomass, in the form of wood and agricultural residues such as wheat straw, is viewed as a low cost alternative feed to sugar and starch. It is also potentially available in far greater quantities than sugar and starch feeds. As such it receives significant attention as a feed material for ethanol production. Like starch, wood and agricultural residues contain polysaccharides. However, unlike starch, while the cellulose fraction of biomass is principally a polymer of easily fermented C₆ sugars, the hemicellulose fraction is principally a polymer of C₅ sugars, with quite different characteristics for recovery, and fermentation of the cellulose and hemicellulose in biomass are bound together in a complex framework of crystalline organic material known as lignin.

There are several different methods of hydrolysis: (i) concentrated sulfuric acid, (ii) dilute sulfuric acid, (iii) nitric acid, and (iv) acid pretreatment followed by enzymatic hydrolysis.

The greatest potential for ethanol production from biomass, however, lies in enzymatic hydrolysis of cellulose. The enzyme cellulase, now used in the textile industry to stone wash denim and in detergents, simply replaces the sulfuric acid in the hydrolysis step. The cellulase can be used at lower temperatures, 30°C–50°C, which reduces the degradation of the sugar. In addition, process improvements now allow simultaneous saccharification and fermentation (SSF). In the saccharification and fermentation process, cellulase and fermenting yeast are combined, so that as sugars are produced, the fermentative organisms convert them to ethanol in the same step.

Once the hydrolysis of the cellulose is achieved, the resulting sugars must be fermented to produce ethanol. In addition to glucose, hydrolysis produces other six-carbon sugars from cellulose and five-carbon sugars from hemicellulose that are not readily fermented to ethanol by naturally occurring organisms. They can be converted to ethanol by genetically engineered yeasts that are currently
available, but the ethanol yields are not sufficient to make the process economically attractive. It also remains to be seen whether the yeasts can be made hardly enough for production of ethanol on a commercial scale.

The fermentation processes to produce propanol and butanol from cellulose are fairly tricky to execute, and the Clostridium acetobutylicum currently used to perform these conversions produces an extremely unpleasant smell, and this must be taken into consideration when designing and locating a fermentation plant. This organism also dies when the butanol content of whatever it is fermenting rises to 7%. For comparison, yeast dies when the ethanol content of its feedstock hits 14%. Specialized strains can tolerate even greater ethanol concentrations—so-called turbo yeast can withstand up to 16% ethanol. However, if ordinary Saccharomyces yeast can be modified to improve its ethanol resistance, scientists may yet one day produce a strain of the Weizmann organism with a butanol resistance higher than the natural boundary of 7%. This would be useful because butanol has a higher energy density than ethanol, and because waste fiber left over from sugar crops used to make ethanol could be made into butanol, raising the alcohol yield of fuel crops without there being a need for more crops to be planted.

Wet milling and dry milling are the means by which grain and straw fractions are processed into a variety of end products. The processes encompass fermentation and distilling of grains (wheat, rye, or maize). Wet milling starts with water-soaking the grain adding sulfur dioxide to soften the kernels and loosen the hulls, after which it is ground. It uses well-known technologies and allows separation of starch, cellulose, oil, and proteins. Dry milling grinds whole grains (including germ and bran). After grinding, the flour is mixed with water to be treated with liquefying enzymes and, further, cooking the mash to breakdown the starch. This hydrolysis step can be eliminated by simultaneously adding saccharifying enzymes and fermenting yeast to the fermenter (simultaneous saccharification and fermentation).

After fermentation, the mash (called beer) is sent through a multicolumn distillation system, followed by concentration, purification, and dehydration of the alcohol. The residue mash (stillage) is separated into a solid (wet grains) and liquid (syrup) phase that can be combined and dried to produce distiller’s dried grains with soluble constituents, to be used as cattle feed. Its nutritional characteristics and high vegetable fiber content make distiller’s dried grains with soluble constituents unsuitable for other animal species.

3.4.3 Chemicals from Biomass

The production of biofuels to replace oil and natural gas is in active development, focusing on the use of cheap organic matter (usually cellulose, agricultural and sewage waste) in the efficient production of liquid and gas biofuels which yield high net energy gain. The carbon in biofuels was recently extracted from atmospheric carbon dioxide by growing plants, so burning it does not result in a net increase of carbon dioxide in the earth’s atmosphere. As a result, biofuels are seen by many as a way to reduce the amount of carbon dioxide released into the atmosphere by using them to replace nonrenewable sources of energy.

3.4.3.1 Gaseous Products

Most biomass materials are easier to gasify than coal because they are more reactive with higher ignition stability. This characteristic also makes them easier to process thermochemically into higher-value fuels such as methanol or hydrogen. Ash content is typically lower than for most coals, and sulfur content is much lower than for many fossil fuels. Unlike coal ash, which may contain toxic metals and other trace contaminants, biomass ash may be used as a soil amendment to help replenish nutrients removed by harvest. A few biomass feedstocks stand out for their peculiar properties, such as high silicon or alkali metal contents—these may require special precautions for harvesting, processing, and combustion equipment. Note also that mineral content can vary as a function of soil type and the timing of feedstock harvest. In contrast to their fairly
uniform physical properties, biomass fuels are rather heterogeneous with respect to their chemical elemental composition.

Biogas contains methane and can be recovered in industrial anaerobic digesters and mechanical biological treatment systems. Landfill gas is a less clean form of biogas which is produced in landfills through naturally occurring anaerobic digestion. Unfortunately, methane is a potent greenhouse gas and should not be allowed to escape into the atmosphere.

When biomass is heated with no oxygen or only about one-third the oxygen needed for efficient combustion (amount of oxygen and other conditions determine if biomass gasifies or pyrolyzes), it gasifies to a mixture of carbon monoxide and hydrogen (synthesis gas, syngas). Combustion is a function of the mixture of oxygen with the hydrocarbon fuel. Gaseous fuels mix with oxygen more easily than liquid fuels, which in turn mix more easily than solid fuels. Syngas, therefore, inherently burns more efficiently and cleanly than the solid biomass from which it was made.

Producing gas from biomass consists of the following main reactions, which occur inside a biomass gasifier (i) drying—biomass fuels usually contain 10–35% w/w moisture and when biomass is heated to 100°C (212°F), the moisture is converted into steam, (ii) pyrolysis—after drying, as heating continues, the biomass undergoes pyrolysis which involves thermal decomposition of the biomass without supplying any oxygen and, as a result, the biomass is decomposed or separated into gases, liquids, and solids, (iii) oxidation in which air is introduced into the gasifier after the decomposition process and during oxidation, which takes place at temperatures in the order of 700°C–1,400°C (1,290°F–2,550°F), charcoal, or the solid carbonized fuel, reacts with the oxygen in the air to produce carbon dioxide and heat, and (iv) reduction that occurs at higher temperatures and under reducing conditions, that is when not enough oxygen is available, the following reactions take place forming carbon dioxide, hydrogen, and methane:

\[
\begin{align*}
C + CO_2 & \rightarrow 2CO \\
C + H_2O & \rightarrow CO + H_2 \\
CO + H_2O & \rightarrow CO_2 + H_2 \\
C + 2H_2 & \rightarrow CH_4
\end{align*}
\]

Biomass gasification can thus improve the efficiency of large-scale biomass power facilities such as those for forest industry residues and specialized facilities such as black liquor recovery boilers of the pulp and paper industry, both major sources of biomass power. Like natural gas, syngas can also be burned in gas turbines, a more efficient electrical generation technology than steam boilers to which solid biomass and fossil fuels are limited.

### 3.4.3.2 Liquid Products

Ethanol is the predominant chemical produced from crops and has been used as fuel in the many countries such as United States since at least 1908. There are three well-known methods to convert biomass into ethanol: (i) direct fermentation of sugar/starch-rich biomass, such as sugar cane, sugar beet, or maize starch to ethanol, in which microorganisms convert carbohydrates to ethanol under anaerobic conditions; (ii) hydrolysis of lignocellulosic biomass (e.g., agricultural waste, wheat, and wood), followed by fermentation to ethanol. Here, again microorganisms convert carbohydrates to ethanol under anaerobic conditions; and (iii) gasification of lignocellulosic biomass, followed by either fermentation or chemical catalysis to ethanol.

Currently, the production of ethanol by fermentation of corn-derived carbohydrates is the main technology used to produce liquid fuels from biomass resources. Furthermore, amongst different biofuels, suitable for application in transport, bioethanol and biodiesel seem to be the most feasible ones at present. The key advantage of bioethanol and biodiesel is that they can be mixed with
conventional petrol and diesel, respectively, which allows using the same handling and distribution infrastructure. Another important strong point of bioethanol and biodiesel is that when they are mixed at low concentrations (≤10% bioethanol in petrol and ≤20% biodiesel in diesel), no engine modifications are necessary.

Biologically produced alcohols, most commonly ethanol and methanol, and less commonly propanol and butanol are produced by the action of microbes and enzymes through fermentation. Methanol is a colorless, odorless, and nearly tasteless alcohol and is also produced from crops and is also used as a fuel. Methanol, like ethanol, burns more completely but releases as much or more carbon dioxide than its gasoline counterpart.

Propanol and butanol are considerably less toxic and less volatile than methanol. In particular, butanol has a high flashpoint of 35°C, which is a benefit for fire safety, but may be difficult for starting engines in cold weather.

Biodiesel is a diesel-equivalent fuel derived from biological sources (such as vegetable oils) which can be used in unmodified diesel engine vehicles. It is, thus, distinguished from the straight vegetable oils or waste vegetable oils used as fuels in some diesel vehicles. In the current context, biodiesel refers to alkyl esters made from the transesterification of vegetable oils or animal fats. Biodiesel fuel is a fuel made from the oil of certain oilseed crops such as soybean, canola, palm kernel, coconut, sunflower, safflower, corn, and a hundreds of other oil-producing crops. The oil is extracted by the use of a press and then mixed in specific proportions with other agents, which causes a chemical reaction. The results of this reaction are two products, biodiesel and soap. After a final filtration, the biodiesel is ready for use. After curing, the glycerin soap that is produced as a byproduct can be used as is, or can have scented oils added before use. In general, biodiesel compares well to petroleum-based diesel (Lotero et al., 2006). Pure biodiesel fuel (100% esters of fatty acids) is called B100. When blended with diesel fuel the designation indicates the amount of B100 in the blend, e.g., B20 is 20% v/v B100 is 80% v/v diesel, and B5 used in Europe contains 5% v/v of B100 in diesel fuel (Pinto et al., 2005).

Hydrocarbon derivatives are products from various plant species belonging to different families, which convert a substantial amount of photosynthetic products into latex. The latex of such plants contains liquid hydrocarbon derivatives of high molecular weight (10,000). These hydrocarbon derivatives can be converted into high-grade transportation fuel (i.e., petroleum). Therefore, hydrocarbon-producing plants are called petroleum plants or petroplants and their crop as petrocrop. Natural gas is also one of the products obtained from hydrocarbon derivatives. Thus, petroleum plants can be an alternative source for obtaining petroleum to be used in diesel engines. Normally, some of the latex-producing plants of families Euphorbiaceae, Apocynaceae, Asclepiadaceae, Sapotaceae, Moraceae, Dipterocarpaceae, etc. are petroplants. Similarly, sunflower (family Composiae), Hardwickia pinnata (family Leguminosae) are also petroplants. Some algae also produce hydrocarbon derivatives.

However, hydrocarbon derivatives, as such, are not usually produced from crops, there being insufficient amount of the hydrocarbon derivatives present in the plant tissue to make the process economical. However, biodiesel is produced from crops thereby offering an excellent renewable fuel for diesel engines.

Bio-oil is a product that is produced by a totally different process than that used for biodiesel production. The process (fast pyrolysis, flash pyrolysis) occurs when solid fuels are heated at temperatures between 350°C and 500°C (570°F–930°F) for a very short period of time (<2 s. The bio-oils currently produced are suitable for use in boilers for electricity generation. In another process, the feedstock is fed into a fluidized bed (at 450°C–500°C) and the feedstock flashes and vaporizes. The resulting vapors pass into a cyclone where solid particles, char, are extracted. The gas from the cyclone enters a quench tower where they are quickly cooled by heat transfer using bio-oil already made in the process. The bio-oil condenses into a product receiver and any non-condensable gases are returned to the reactor to maintain process heating. The entire reaction from injection to quenching takes only two seconds.
3.4.3.3 Solid Products

Examples of solid chemicals from biomass feedstocks include wood and wood-derived charcoal and dried dung, particularly cow dung. One widespread use of such fuels is in home cooking and heating. The biofuel may be burned on an open fireplace or in a special stove. The efficiency of this process may vary widely, from 10% for a well-made fire (even less if the fire is not made carefully) up to 40% for a custom-designed charcoal stove. Inefficient use of fuel is a cause of deforestation (though this is negligible compared to deliberate destruction to clear land for agricultural use), but more importantly it means that more work has to be put into gathering fuel, thus the quality of cooking stoves has a direct influence on the viability of biofuels.

Investigation of the products produced during thermal decomposition (pyrolysis) is worthy of investigation since the potential to produce lower molecular weight feedstocks for a petrochemical plant is high.

3.5 WASTE

It would be remiss not to mention another potential feedstock for the production of chemicals—waste material that is not included under the general category of biomass (John and Singh, 2011). Non-biomass waste is a byproduct of life and civilization; it is the material that remains after a useful component has been consumed. From an economic perspective, waste is a material involved in life or technology whose value today is less than the cost of its utilization. From a regulatory viewpoint, waste is anything discarded or that can no longer be used for its original purpose.

Waste is the general term; though the other terms are used loosely as synonyms, they have more specific meanings. The term solid waste includes not only solid materials, but also liquid and gases. Domestic waste (also known as rubbish, garbage, trash, or junk) is unwanted or undesired material. Rubbish or trash are mixed household waste including paper and packaging; food waste or garbage (North America) is kitchen and table waste; and junk or scrap is metallic or industrial material.

The thermal pyrolysis of plastic wastes produces a broad distribution of hydrocarbons, from methane to waxy products. This process takes place at high temperatures. The gaseous compounds generated can be burned out to provide the process heat requirements, but the overall yield of valuable gasoline-range hydrocarbons is poor, so that the pyrolysis process as a means for feedstock recycling of the plastic waste stream is rarely practiced on an industrial scale at present (Predel and Kaminsky, 2000; Kaminsky and Zorriqueta, 2007). In contrast, thermal cracking at low temperatures is usually aimed at the production of waxy oil fractions, which may be used in industrial units for steam cracking and in fluid catalytic cracking units (Aguado et al., 2002). An alternative to improve the yield of naphtha from the pyrolysis of plastic waste is to introduce suitable catalysts. High conversion and interesting product distribution is obtained when plastics are cracked over zeolites (Hernandez et al., 2007). Moreover, the catalytic cracking of polymers has proven itself to be a very versatile process, since a variety of products can be obtained depending on parameters such as (i) the catalyst, (ii) the polymer feedstocks, (iii) the reactor type, and (iv) the process parameters, such as temperature, pressure, and residence time of the feedstock in the hot zone, as well as product removal from the hot zone (Aguado and Serrano, 1999; Demirbaş, 2004; Scheirs and Kaminsky, 2006. Marcilla et al., 2008; Al-Salem et al., 2009; Sarker et al., 2012).

In addition, urban waste (domestic and industrial) has considerable promise as a feedstock for gasification because it contains relatively more lignin, which biological processes cannot convert. Such waste is abundant in most countries and can be harnessed for production of fuels and petrochemical intermediates. Knowing the potential of the waste for gasification and subsequent fuel production is essential for reducing pressure on traditional energy sources.

Also, discarded tires can be reduced in size by grinding, chipping, pelletizing, and passed through a classifier to remove the steel belting after which the chips are pyrolyzed for 1 h at a temperature of 300°C–500°C (570°F–930°F) and then heated for 2 h in a closed retort to yield gas, distillable,
Coal, Oil Shale, and Biomass

and char. Discarded tires can also be shredded to 25 mm and ground to 24 mesh as a feed-preparation step for occidental flash pyrolysis that involves flash pyrolysis and product collection. The pyrolytic reaction occurs without the introduction of hydrogen or using a catalyst. This yields a gaseous stream that is passed to a quench tower from which fuel oil and gas (recycled to char fluidized and pyrolysis reactor as a supplemental fuel) and carbon black (35% w/w) is produced. In the Nippon Zeon process, crushed tire chips undergo fluidized thermal cracking (fluidized bed, 400°C–600°C, 750°F–1,110°F), which yields a gaseous stream that is passed to a quench tower from which gas and distillable oil is produced. All of the end products produced could be used directly as a supplemental fuel source at the plant or sent off-site for petrochemical manufacture.

REFERENCES


