Chapter 7
Biorefineries

7.1 Introduction

Energy needs are increasing continuously because of increases in industrialization and population. The growth of the world's energy demand raises urgent problems. The larger part of petroleum and natural gas reserves is located within a small group of countries. Today's energy system is unsustainable because of equity issues as well as environmental, economic, and geopolitical concerns that have implications far into the future. Bioenergy is one of the most important components of greenhouse-gas-emissions mitigation and fossil–fuel replacement (Goldemberg 2000; Dincer 2008). Renewable energy is one of the most efficient ways to achieve sustainable development.

Plants use photosynthesis to convert solar energy into chemical energy, which is stored in the form of oils, carbohydrates, proteins, etc. This plant energy is converted into biofuels. Hence biofuels are primarily a form of solar energy. For biofuels to succeed at replacing large quantities of petroleum fuel, the feedstock availability needs to be as high as possible. There is an urgent need to design integrated biorefineries that are capable of producing transportation fuels and chemicals.

In recent years, the recovery of liquid transportation biofuels from biorenewable feedstocks has became a promising method. The biggest difference between biorenewable and petroleum feedstocks is oxygen content. Biorenewables have oxygen levels from 10 to 44%, while petroleum has essentially none, making the chemical properties of biorenewables very different from those of petroleum (Demirbas 2008; Balat 2009). For example, biorenewable products are often more polar; some easily entrain water and can therefore be acidic.

There are two global transportation fuels – gasoline and diesel fuel. The main transportation fuels that can be obtained from biomass using different processes are sugar ethanol, cellulosic ethanol, grain ethanol, biodiesel, pyrolysis liquids, green diesel, green gasoline, butanol, methanol, syngas liquids, biohydrogen, algae diesel, algae jet fuel, and hydrocarbons. Renewable liquid biofuels for transportation have recently attracted considerable attention in various countries around the world be-

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cause of their renewability, sustainability, widespread availability, and biodegradability, as well as for their potential role in regional development, rural manufacturing jobs, and the reduction of greenhouse gas emissions (Demirbas 2008). Transportation fuels, both petroleum-based and biorenewable, are given in Figure 7.1.

The term biofuel or biorenewable fuel (refuel) is referred to as solid, liquid, or gaseous fuels that are predominantly produced from biomass. Liquid biofuels being considered the world over fall into the following categories: (a) bioalcohols, (b) vegetable oils and biodiesels, and (c) biocrude and synthetic oils. Biofuels are important because they replace petroleum fuels. It is expected that the demand for biofuels will rise in the future. Biofuels are substitute fuel sources for petroleum; however, some still include a small amount of petroleum in the mixture. It is generally considered that biofuels address many concerns, including sustainability, reduction of greenhouse gas emissions, regional development, social structure and agriculture, and supply security. Biofuels, among other sources of renewable energy, are attracting interest as alternative to fossil diesel. With an increasing number of governments now supporting this cause in the form of mandates and other policy initiatives, the biofuel industry is poised to grow at a phenomenal rate (Balat 2007; Demirbas 2002, 2003, 2007; Demirbas and Karslioglu 2007; Khoiyangbam 2008; Chhetri and Islam 2008).

Policy drivers for biorenewable liquid biofuels have attracted support for rural development and economic opportunities for developing countries (Keskin 2009). The EU ranks third in biofuel production worldwide, behind Brazil and the USA. In Europe, Germany is the largest and France the second largest producer of biofuels.

The term modern biomass is generally used to describe traditional biomass use through efficient and clean combustion technologies and sustained supply of

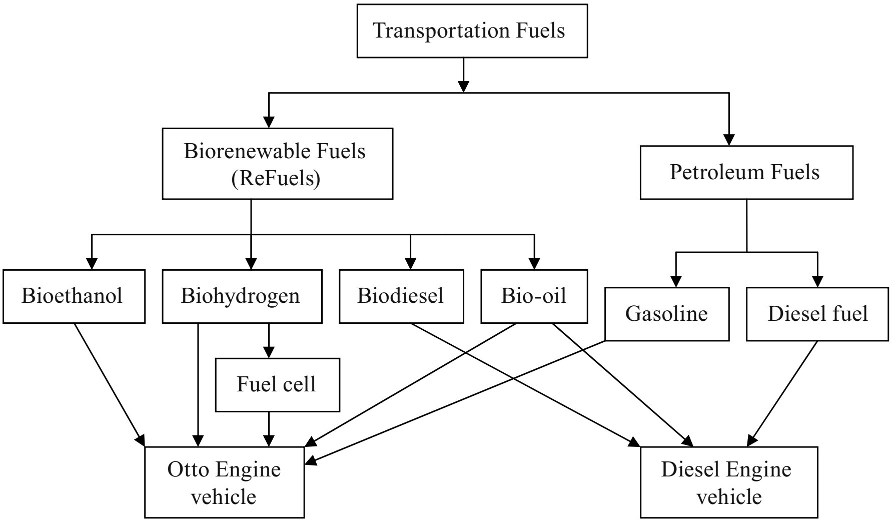


Figure 7.1 Transportation fuels

biomass resources, environmentally sound and competitive fuels, heat, and electricity using modern conversion technologies. Biomass, as an energy source, has two striking characteristics. First, biomass is the only renewable organic resource to exist in abundance. Second, biomass fixes carbon dioxide in the atmosphere by photosynthesis. Direct combustion and cofiring with coal for electricity production from biomass holds great promise. Biomass thermochemical conversion technologies such as pyrolysis and gasification are certainly not the most important options at present; combustion is responsible for over 97% of the world's bioenergy production. Ethanol and fatty acid (m)ethylester (biodiesel), as well as diesel produced from biomass by Fischer–Tropsch synthesis (FTS), are modern biomass-based transportation fuels. Liquid transportation fuels can be economically produced by biomass-integrated gasification Fischer–Tropsch (BIG-FT) processes. Modern biomass produced in a sustainable way excludes traditional uses of biomass as fuel wood and includes electricity generation and heat production, as well as transportation fuels, from agricultural and forest residues and solid waste. On the other hand, traditional biomass is produced in an unsustainable way and is used as a noncommercial source – usually with very low efficiencies for cooking in many countries. Biomass energy potentials and current use in different regions are given in Table 7.1 (Parikka 2004).

Like a petroleum refinery, a biorefinery uses every component of the biomass raw material to produce usable products. Bio-based products are prepared for economic use by an optimal combination of different methods and processes (physical, chemical, biological, and thermal). Therefore, basic biorefinery concepts must be developed. A biorefinery, as a new approach, is a processing plant where biomass feedstocks are converted and extracted into a spectrum of valuable products. Biorefining refers to fractionating biomass into various separated products that possibly undergo further chemical, biochemical, biological, and thermochemical processing and separation. The molecules produced by biorefining can be obtained using thermal, chemical, mechanical, enzymatic, or microbial processes, and they can be used in transport fuels, therapeutics, food additives, or as secondary chemicals with a range of applications. By coproducing chemicals, the production costs of secondary energy carriers (fuels, heat, power) could potentially become more profitable, especially

Table 7.1 Biomass energy potentials and current use in different regions

Biomass potential	North America	Latin America	Asia	Africa	Europe	Middle East	Former USSR	World
Woody biomass	12.8	5.9	7.7	5.4	4.0	0.4	5.4	41.6
Energy crops	4.1	12.1	1.1	13.9	2.6	0.0	3.6	37.4
Straw	2.2	1.7	9.9	0.9	1.6	0.2	0.7	17.2
Other	0.8	1.8	2.9	1.2	0.7	0.1	0.3	7.6
Potential sum (EJ/a)	19.9	21.5	21.4	21.4	8.9	0.7	10.0	103.8
Use (EJ/a)	3.1	2.6	23.2	8.3	2.0	0.0	0.5	39.7
Use/potential (%)	16	12	108	39	22	7	5	38

when biorefining is integrated into the existing chemical, material, and power industries. Coproduction of bioproducts, materials, chemicals, transportation fuels, power, or heat in technically, economically, and ecologically fully optimized integrated biorefinery systems will be required.

7.2 Definitions of Biorefinery

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and value-added chemicals from biomass. The biorefinery concept is analogous to today's crude oil refinery, which produces multiple fuels and products from petroleum. Biorefinery refers to the conversion of biomass feedstock into a host of valuable chemicals and energy with minimal waste and emissions. In a broad definition, biorefineries process all kinds of biomass (all organic residues, energy crops, and aquatic biomass) into numerous products (fuels, chemicals, power and heat, materials, and food and feed). Figure 7.2 shows a schematic diagram of a biorefinery.

A biorefinery is a conceptual model for future biofuel production where both fuels and high-value coproduct materials are produced. Biorefineries can simultaneously produce biofuels as well as bio-based chemicals, heat, and power. Biorefiner-

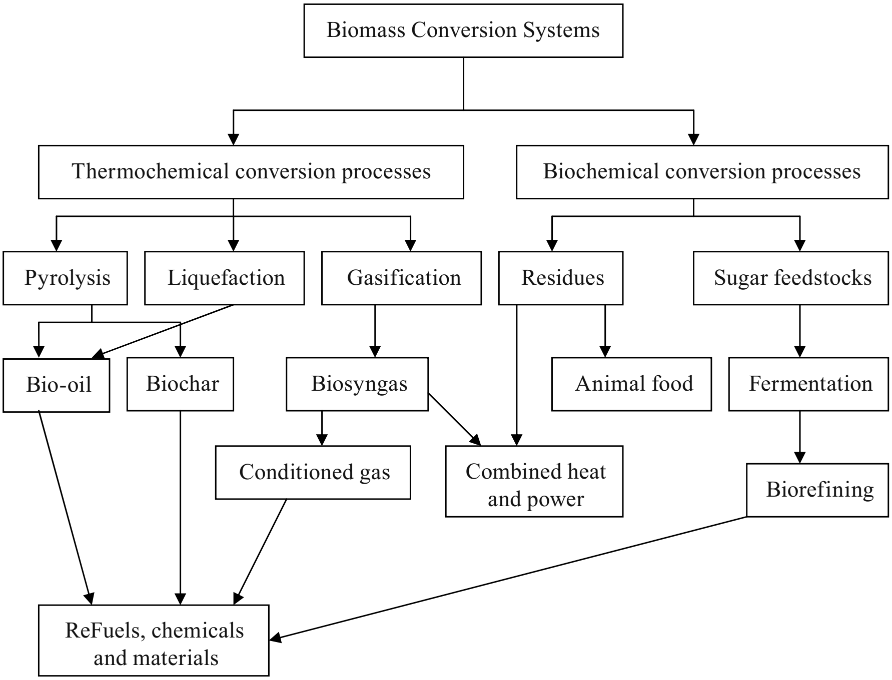


Figure 7.2 Biorefinery concept

ies present more cost-effective options where bio-based chemicals are coproducts of liquid fuel. Future biorefineries would be able to mimic the energy efficiency of modern oil refining through extensive heat integration and coproduct development. Heat that is released from some processes within the biorefinery could be used to meet the heat requirements for other processes in the system (WI 2007).

Reliable designs of equipment for the thermochemical stages of biomass conversion have yet to be widely demonstrated and shown capable of continuously producing synthesis gas of the required quality. Synthesis gas has to be free of nitrogen; this requires the use of oxygen (expensive), a pyrolytic process optimized for gas, or a multistage process. The main nontechnical barriers to acceptance of liquid biofuels, especially in the transport sector, relate to the costs of production, available markets, taxation policies, and legislation, as well as blending and distribution. From an economic point of view the use of agricultural crops, without subsidy, is too expensive to produce either bioethanol or biodiesel at a price competitive with untaxed petrol or diesel fuel, while processes for using lower cost lignocellulosic materials have not been perfected. There are a number of pilot-scale and demonstration plants operating, under development, or planned with fully commercial developments not expected for another decade or two (GBRP 2007).

Developed and developing countries clearly have different goals in the development of biomass energy. Biomass energy is promoted in developed countries as a replacement for fossil fuels, particularly in the transportation sector, whereas its use serves basic livelihood purposes in developing countries. Combining higher-value products with higher-volume energy production and employing any combination of conversion technologies has the greatest potential for making fuels, chemicals, materials, and power from biomass competitive. Obtaining modern biofuels, biopower, and bioproducts from biomass can be realized only in integrated biorefineries. This chapter reviews current biorenewable fuel valorization facilities as well as the future importance of biorefineries. The development of biorefinery technologies is important, and these technologies are also very promising.

Broadly speaking, the term biorefinery can be thought of as a concept of multiple products from various biomass feedstocks. A biorefinery processes biomass into value-added product streams. In theory, anything that uses biomass and makes more than one product is a biorefinery. A biorefinery is analogous to a petroleum refinery processing a range of crude oils. This very simple definition captures a wide range of existing, emerging, and advanced process concepts. Examples of existing biorefineries include corn processors and pulp and paper mills.

The concept is analogous to a combined use of fluid catalytic cracking, thermal cracking, and hydrocracking technology to convert the higher-boiling-range fractions of crude oil into more useful lower-boiling-range products. Just as few petroleum refineries use all available conversion technologies, biorefineries too will use only those technology platforms that are most cost effective for converting a certain type of biomass into a certain collection of desired end products. For crops and agricultural waste, it would be better to convert the biomass into bio-oil near the farm and transport the high-density bio-oil to a central facility for processing rather than transporting the low-density biomass.

The biorefinery concept attempts to apply to biomass conversion the methods that have been applied to the refining of petroleum. The goal is to maximize the value of the products obtained from the biomass. The goal of the integrated biorefinery program area is to support the establishment of integrated biorefineries through partnerships with industry and academia.

7.2.1 Main Technical and Nontechnical Gaps and Barriers to Biorefineries

There are a lot of technical and nontechnical gaps and barriers related to the implementation and commercialization of the biorefinery. Current technical barriers with the use of energy crops are associated with the cost of production and difficulties in harvesting and storing the material grown, especially for annual or other crops that have to be harvested within a narrow time period in the autumn. Transportation costs are of prime importance when calculating the overall cost of biomass; hence local or regional production of biomass is most favorable. Other technical problems associated with growing energy crops include provision of nutrients and control of pests and disease.

The major nontechnical barriers are restrictions or prior claims on use of land (food, energy, amenity use, housing, commerce, industry, leisure, or designated areas of natural beauty, special scientific interest, etc.), as well as the environmental and ecological effects of large areas of monoculture. For example, vegetable oils are a renewable and potentially inexhaustible source of energy with an energy content close to that of diesel fuel. On the other hand, extensive use of vegetable oils may cause other significant problems such as starvation in developing countries. Vegetable oil fuels are not acceptable because they were more expensive than petroleum fuels.

In addition to the technical challenges of commercializing advanced biorefineries, there are also large infrastructure barriers. These barriers are associated with the development of new agricultural infrastructure for the collection and storage of crop wastes. An integrated feedstock supply system must be developed that can supply the feedstock needs in a sustainable fashion at a reasonable cost. Infrastructure issues could be as significant as the technical issues when considering overall production costs.

7.3 Historical Perspective

The process of converting biorenewables into useful and higher-value compounds is not new. For example, sugar cane has been used in the production of bioethanol since 6000 BC (Demirbas 2009). Lactic acid was first discovered by C. W. Scheele in 1780. Its production was developed into an industrial-level fermentation process by A. Boehringer in Germany in 1895, with subsequent uses in the food, leather, and textile industries. Even to this day, lactic acid is used as a preservative, flavor enhancer, and aciduant in the food industry.

Ethanol has been used by humans since prehistory as the intoxicating ingredient of alcoholic beverages. The ancient Egyptians produced alcohol by naturally fermenting vegetative materials. Also in ancient times, the Chinese discovered the art of distillation, which increases the concentration of alcohol in fermented solutions. Dried residues on 9000-year-old pottery have been found in China. Its isolation as a relatively pure compound was first achieved by Persian alchemist Zakariya Razi. Ethanol was first prepared synthetically in 1826 through the independent efforts of Henry Hennel in Great Britain. Ethanol was used as lamp fuel in the USA as early as 1840. In the 1970s, however, the ethanol industry began to reemerge when ethanol was used as a fuel extender during gasoline shortages caused by the OPEC oil embargoes.

Ethanol has been used in Germany and France as early as 1894 by the then-incipient industry of internal combustion engines. Brazil has utilized ethanol as a fuel since 1925. By that time, the production of ethanol was 70 times bigger than the production and consumption of petroleum.

The emergence of transesterification can be dated back to as early as 1846 when Rochieder described glycerol preparation through the ethanolysis of castor oil. Since that time alcoholysis has been studied in many parts of the world. Transesterification of a vegetable oil was conducted as early as 1853, by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional. Life for the diesel engine began in 1893 when the famous German inventor Dr. Rudolph Diesel published a paper entitled “The theory and construction of a rational heat engine.” What the paper described was a revolutionary engine in which air would be compressed by a piston to a very high pressure, thereby causing a high temperature. Dr. R. Diesel designed the original diesel engine to run on vegetable oil.

Dr. Diesel’s primary model, a single 3-m iron cylinder with a flywheel at its base, ran on its own power for the first time in Augsburg, Germany on 10 August 1893. (In remembrance of this event, 10 August has been declared International Biodiesel Day.) This engine stood as an example of Diesel’s vision because it was powered by peanut oil, a biofuel, though not strictly biodiesel, since it was not transesterified. He believed that the utilization of a biomass fuel was the real future of his engine. In a 1912 speech, Dr. Diesel said, “The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time.”

The use of vegetable oils as an alternative renewable fuel competing with petroleum was proposed in the early 1980s. The advantages of vegetable oils as diesel fuel are its portability, widespread availability, renewability, higher heat content (about 88% of no. 2 petroleum diesel fuel), lower sulfur content, lower aromatic content, and biodegradability. The energy supply concerns of the 1970s renewed interest in biodiesel, but commercial production did not begin until the late 1990s.

Since the 1980s, biodiesel plants have opened in many European countries, and some cities have run buses on biodiesel, or blends of petro and bio diesels. More recently, Renault and Peugeot have approved the use of biodiesel in some of their truck engines. Recent environmental and domestic economic concerns have prompted a resurgence in the use of biodiesel throughout the world. In 1991, the European Community (EC) proposed a 90% tax deduction for the use of biofuels, including biodiesel. Biodiesel plants are now being built by several companies in Europe; each of these plants will produce up to 5.67 million liters of fuel per year. The EU accounted for nearly 89% of all biodiesel production worldwide in 2005.

A historical outline of the technology and industrial resources related to biodiesel must include discussions on the beginnings of sugar production, starch hydrolysis, wood saccharification, formation and separation of furfural, cellulose and pulp production, synthesis of levulinic acid, lipids, vanillin from lignin, and lactic acid fermentation. During the industrial revolution, coal became the energy source of preference, displacing biomass fuels such as wood. Since then a steady migration toward fossil fuels has continued, moving further away from biomass, not only for energy but also for sources of chemicals used to make everyday items. An excellent example of this is furfural, which can be obtained from oat hulls. Some current aspects of biorefinery research and development since the early 1990s have been presented, revealing that integrated processes, biomass refinery technology, and biorefinery technology have become objects of research and development. Table 7.2 shows the main biorefinery demonstration projects: plant capacity, planned or under construction.

Many of the currently used bio-based industry products are the results of direct physical or chemical treatment and processing of biomass: cellulose, starch, oil, protein, lignin, and terpenes. Also, with the help of biotechnological processes and methods, feedstock chemicals, such as ethanol, buthanol, acetone, lactic and itaconic acids, and amino acids, are produced.

The topic of biorefineries as a means of processing industrial material and efficiently utilizing renewable products is well known and applied worldwide, in almost every developed and emerging country. This trend is motivated by the rising cost of oil (petroleum) and the need to move away from petrochemical-based systems. The sustainability of integrated biorefining systems includes aspects of agriculture/forestry ecosystem modeling and analysis, as well as technical and economic considerations underlining the importance of biorefineries and the growing demand for new products.

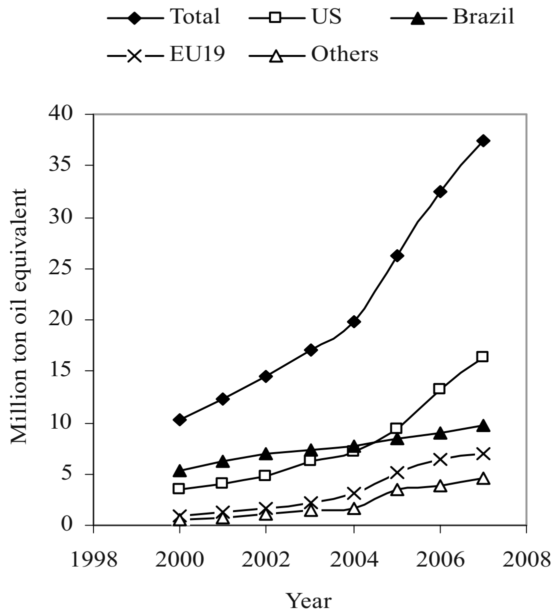
Furthermore, the technology of sugar refining, starch production, and oil milling, the separation of proteins as feed, and the extraction of chlorophyll for industrial use with alfalfa as raw material were of great historical importance. But processes like wet grinding of crops and biotechnological processes such as the production of ethanol as well as acetic, lactic, and citric acids also used to be of fundamental importance in the 19th and 20th centuries. Figure 7.3 shows global trends in biofuel production by region.

Today's biorefinery technologies are based on (a) utilization of the whole plant or complex biomass and (b) the integration of traditional and modern processes for utilization of biological raw materials (Kamm *et al.* 2005). In the 19th and early 20th centuries, large-scale utilization of renewable resources was focused on pulp and paper production from wood, saccharification of wood, nitration of cellulose

Table 7.2 Biorefinery demonstration projects: plant capacity, planned or under construction

Name	Location	Participants	Annual capacity, million liters
Iogen	Shelley ID, USA	Iogen Corporation, Goldman Sachs, Royal Dutch Shell Oil Company; others	68 (in first plant) 945 (in future plants) cellulosic ethanol
BlueFire Ethanol	Lancaster, CA, USA	BlueFire Ethanol Fuels, Inc.	121 Cellulosic ethanol
Poet	Sioux Falls, SD, USA	Broin Companies	246 Corn ethanol
Ecofin, LLC	Washington County, KY, USA	University of Cincinnati, University of Kentucky, Alltech, Inc.	5 Corncob ethanol
ICM, Incorporated	St. Joseph, MO, USA	AGCO Eng; NCAUR-ARS-Peoria; CERES, Inc.; Edens. Sys. Corp.; Novozymes NA, Inc.; Sun EtOH, Inc.; others	5.7 Lignocellulosic ethanol
Lignol Innovations	Canada's Lignol Energy Corporation	Commerce City, CO, USA	9.55 Cellulosic ethanol
Royal Nedalco	Rotterdam Area, Netherlands	Ethanol Reach Association	227 Cellulosic ethanol
Mascoma	Rome, NY, USA	Mascoma Corporation, DuPont-Danisco	1.9 Cellulosic ethanol
Pacific Ethanol	Boardman, OR, USA	Pacific Ethanol, Inc.	10.2 Lignocellulosic ethanol
Abengoa Bioenergy	Colwich, KS, USA	Abengoa Bioenergy LLL	95 Lignocellulosic ethanol
Verenium	Jennings, LA, USA	Verenium Corporation	5.7 Cellulosic ethanol
RSE Pulp	Old Town, ME, USA	RSE Pulp & Chemical Llc Company	8.7 Cellulosic ethanol
Flambeau	Park Falls, WI, USA	Flambeau LLC	53.7 Lignocellulosic ethanol
NewPage	Wisconsin Rapids, WI, USA	NewPage Corporation	48.4 Biofuels, FT liquids
Choren	Freiberg, Germany	Choren Industries	5.7 Biofuels, FT liquids
Alico	LaBelle, FL, USA	Alico, Inc.; Bioeng. Res., Inc. Fayetteville, AR; Washington Group Intl. of Boise, ID; Emmaus Found., Inc.; others	28,4 Ethanol, electricity, ammonia, hydrogen
Range Fuels	Broomfield, CO, USA	Range Fuels, Inc.	4.5 Biofuels, FT liquids
Flambeau River	Jennings, LA, USA	Flambeau River BioFuels	24.6 Biofuels, FT liquids

Figure 7.3 Global trends in biofuel production by region



for guncotton and viscose silk, production of soluble cellulose for fibers, fat curing, and the production of furfural for Nylon. Advanced biorefineries are envisioned as the foundation of a new bioindustry. By exploiting new chemical, biological, and mechanical technologies, they offer the promise of greatly expanding the use of renewable plant-based materials, as well as a means of transitioning to a more energy-efficient and environmentally sustainable chemical and energy economy.

7.4 Petroleum Refinery and Biorefinery

In 1858, Dr. Abraham Gesner, a Canadian physician and amateur geologist, developed and patented the extraction of a lamp fuel from asphalt rock, which he named kerosene (Nova Scotia Museum 2008). At that time, kerosene, which was an extremely high-value lighting fuel for lamps, was the primary product of petroleum refining. For a while, distillation of kerosene for lamps was the mainstay of the new petroleum industry. Gasoline was merely a byproduct of kerosene production from crude oil, and until the early 1900s there was no significant demand for it. The first petrochemical, aside from carbon black manufactured on an industrial scale, was isopropyl alcohol, made by Standard Oil of New Jersey in 1920.

When a mixture of two liquids of different boiling points is heated to its boiling point, the vapor contains a higher mole fraction of the liquid with the lower boiling point than the original liquid, i.e., the vapor is enriched in the more volatile component. If this vapor is now condensed, the resultant liquid has also been enriched in the more volatile component. This is the principle of batch fractional distillation, and in a distillation column many, many such cycles are performed continuously, allowing almost complete separation of liquid components. A generalized distillation column is shown in Figure 7.4. The first step in the refining of crude oil, whether in a simple or a complex refinery, is the separation of the crude oil into fractions (fractionation or fractional distillation). These fractions are mixtures containing hydrocarbon compounds whose boiling points lie within a specified range.

Crude oil is a complex mixture that is between 50 and 95% hydrocarbon by weight. The first step in refining crude oil involves separating the oil into different hydrocarbon fractions by distillation. An oil refinery cleans and separates the crude oil into various fuels and byproducts, including gasoline, diesel fuel, heating oil, and jet fuel. The main crude oil components are listed in Table 7.3. Since various components boil at different temperatures, refineries use a heating process called distillation to separate the components. For example, gasoline has a lower boiling point than kerosene, allowing the two to be separated by heating to different temperatures. Another important job of the refineries is to remove contaminants from the oil, for example, sulfur from gasoline or diesel to reduce air pollution from the automobile exhausts. After processing at the refinery, gasoline and other liquid products are usually shipped out through pipelines, which are the safest and cheapest way to move large quantities of petroleum across land (Demirbas 2009).

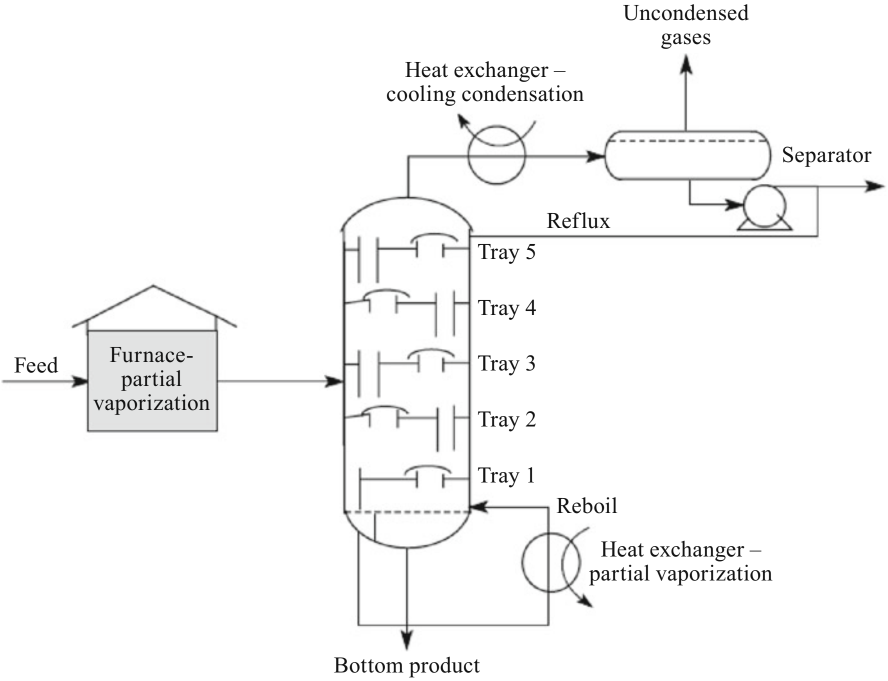


Figure 7.4 A generalized fractional distillation column

Table 7.3 Main crude oil fractions

Component	Boiling range, K	Number of carbon atoms
Natural gas	< 273	C_1 to C_4
Liquefied petroleum gas	231–273	C_3 to C_4
Petroleum ether	293–333	C_5 to C_6
Ligroin (light naphtha)	333–373	C_6 to C_7
Gasoline	313–478	C_5 to C_{12}, and cycloalkanes
Jet fuel	378–538	C_8 to C_{14}, and aromatics
Kerosene	423–588	C_{10} to C_{16}, and aromatics
No. 2 diesel fuel	448–638	C_{10} to C_{22}, and aromatics
Fuel oils	> 548	C_{12} to C_{70}, and aromatics
Lubricating oils	> 673	$> C_{20}$
Asphalt or petroleum coke	Nonvolatile residue	Polycyclic structures

The refining of heavy oil requires extracting and thorough chemical, engineering, and computing processes. Before the actual refining begins, the stored heavy crude oil is cleaned of contaminants such as sand and water.

Industrial distillation is typically performed in large, vertical, steel cylindrical columns known as distillation towers or distillation columns with diameters ranging from about 65 cm to 11 m and heights ranging from about 6 to 60 m or more. To improve the separation, the tower is normally provided inside with horizontal plates or trays, or the column is packed with a packing material. To provide the heat required for the vaporization involved in distillation and also to compensate for heat loss, heat is most often added to the bottom of the column by a reboiler. Large-scale industrial fractionation towers use reflux to achieve more efficient separation of products. Reflux refers to the portion of the condensed overhead liquid product from a distillation tower that is returned to the upper part of the tower. Inside the tower, the downflowing reflux liquid provides cooling and partial condensation of the upflowing vapors, thereby increasing the efficacy of the distillation tower. There are generally 25 to 45 plates or trays in a distillation tower. Each of the plates or trays is at a different temperature and pressure. The stage at the tower bottom has the highest pressure and temperature. Progressing upwards in the tower, the pressure and temperature decrease for each succeeding stage. Another way of improving the separation in a distillation column is to use a packing material instead of trays.

Three major refinery processes change crude oil into finished products: (1) separation, (2) conversion, and (3) purification. The first step is to separate the crude oil into its naturally occurring components. This is known as separation and is accomplished by applying heat through a process called distillation. Separation is performed in a series of distillation towers. The conversion processes have focused on reducing the length of some hydrocarbon chains. The primary purpose of conversion is to convert low valued heavy oil into high valued petrol. For example, catalytic reforming is a conversion process. The purpose of the reformer is to increase the octane number of the petrol blend components. Once crude oil has been through separation and conversion, the resulting products are ready for purification, which is principally sulfur removal. Common process units found in an oil refinery are presented in Table 7.4.

Petroleum refining is somewhat analogous to biorefining. Although biorefineries utilize different processing technologies, they separate and isolate components of biomass for the production of energy fuels, chemicals, and materials. Biorefineries can be designed and built to produce desired outputs from the processing of a wide variety of biorenewable materials. These biorefineries will adopt and integrate a range of materials handling and preprocessing equipment, thermochemical and biochemical conversion technologies, and new extraction and purification sciences to produce a range of intermediate products, while using less energy and reducing effluents and emissions. The scale of the biorefining operations will range from medium-sized to very large (equivalent in size to existing chemical plants and pulp and paper mills). Adoption of biorefineries and related processes and product technologies depends on available research, development, and prevailing regulations during design and construction.

In some ways, biorefineries are analogous to oil refineries. Oil refineries take crude oil and fractionate it into many different useful parts. This is done using a simple chemical distillation process. Biomass, like oil, consists of many different fractions that are separated and made into useful products in biorefineries. However, the processes involved in fractionating biomass are more complex than those used in oil refineries. Another important difference between biorefineries and oil refineries is their size. The term biorefinery was coined to describe future processing complexes that will use renewable agricultural residues, plant-based starch, and lignocellulosic materials as feedstocks to produce a wide range of chemicals, fuels, and bio-based materials. Biorefineries will most likely be limited in size, because biomass must be produced and transported economically from a limited catchment area. In contrast, oil is drilled and transported all over the world for processing.

Biomass can be processed into plastics, chemicals, fuels, heat, and power in a biorefinery. High-value components, for example essential oils, drugs, or fibers, can be recovered as a preprocessing step, with the remaining materials then processed downstream. Processing technologies are most advanced for chemicals and fuels. Biorefineries vary from small single-process plants to large multiprocess sites. Larger biorefineries will be able to integrate different technologies to obtain maximum value from biomass feedstocks.

A biorefinery is an integrated plant producing multiple value-added products from a range of renewable feedstocks. This innovative approach responds to changing markets for traditional forest products as well as new products such as energy, chemicals, and materials. The range of feedstocks, processes, and potential products is large; each combination of feedstock, process, and product is characterized by its own unique combination of technical and economic opportunities, emerging technologies, and barriers.

Table 7.5 shows the classification of biorefineries based on their feedstocks. A forest biorefinery will use multiple feedstocks including harvesting residues, extracts from effluents, and fractions of pulping liquors to produce fiber, energy, chemicals, and materials. A lignocellulosic-based biorefining strategy may be supported

Table 7.4 Common process units found in an oil refinery

	Unit	Treatment
1	Desalter	Washes out salt from the crude oil before it enters the atmospheric distillation unit
2	Atmospheric distillation	IDdistills crude oil into fractions
3	Vacuum distillation	Further distills residual bottoms after atmospheric distillation
4	Naphtha hydrotreater	Uses hydrogen to desulfurize naphtha from atmospheric distillation
5	Catalytic reformer	Used to convert the naphtha-boiling-range molecules into higher-octane reformer product (reformate)
6	Distillate hydrotreater	Desulfurizes distillates (such as diesel) after atmospheric distillation
7	Fluid catalytic cracker (FCC)	Upgrades heavier fractions into lighter, more valuable products
8	Hydrocracker	Uses hydrogen to upgrade heavier fractions into lighter, more valuable products
9	Visbreaking	Upgrades heavy residual oils by thermally cracking them into lighter, more valuable reduced-viscosity products
10	Merox	Treats LPG, kerosene, or jet fuel by oxidizing mercaptans into organic disulfides
11	Coking	Converts very heavy residual oils into gasoline and diesel fuel, leaving petroleum coke as a residual product
12	Alkylation	Produces high-octane component for gasoline blending
13	Dimerization	Converts olefins into higher-octane gasoline blending components
14	Isomerization	Converts linear molecules into higher-octane branched molecules for blending into gasoline
15	Steam reforming	Produces hydrogen for hydrotreaters or hydrocracker
16	Liquefied gas storage	For propane and similar gaseous fuels at pressure sufficient to maintain in liquid form
17	Storage tanks	For crude oil and finished products, usually cylindrical, with some sort of vapor emission control
18	Amine gas and tail gas treatment	For converting hydrogen sulfide from hydrodesulfurization into elemental sulfur
19	Utility units	Such as cooling towers for circulating cooling water, boiler plants for steam generation
20	Wastewater collection and treating	Converts wastewater into water suitable for reuse or for disposal
21	Solvent refining	Uses solvent such as cresol or furfural to remove unwanted, mainly asphaltenic materials from lubricating oil stock
22	Solvent dewaxing	For removing the heavy waxy constituents of petroleum from vacuum distillation products

Table 7.5 Classification of biorefineries based on their feedstocks

	Feedstocks	Products
Green biorefinery	Grasses, green plants	Ethanol
Cereal biorefinery	Starch crops, sugar crops, grains	Bioethanol
Oilseed biorefinery	Oilseed crops, oil plants	Vegetable oils, biodiesels
Forest biorefinery	Forest harvesting residues, barks, sawdust, pulping liquors, fibers	Fuels, energy, chemicals, materials
Lignocellulosic biorefinery	Agricultural wastes, crop residues, urban wood wastes, industrial organic wastes	Lignocellulosic ethanol, bio-oil, gaseous products

by biomass reserves, created initially with residues from wood product processing or agriculture. Biomass reserves should be used to support first-generation biorefining installations for bioethanol production, development of which will lead to the creation of future high-value coproducts (Mabee *et al.* 2006).

Biorefineries can be classified based on their production technologies: first-generation biorefineries (FGBRs), second-generation biorefineries (SGBRs), third-generation biorefineries (TGBRs), and fourth-generation biorefineries.

The FGBRs refer to biofuels made from sugar, starch, vegetable oils, or animal fats using conventional technology. Table 7.6 shows the classification of biorefineries based on their generation technologies. SGBRs and TGBRs are also called advanced biorefineries. SGBRs made from nonfood crops, wheat straw, corn, wood, and energy crop using advanced technology.

Sugar and vegetables are used and converted into bioalcohols and biodiesel in FGBRs. The transition from FGBRs to SGBRs will mark a qualitative leap. Lignocellulosic residues such as sugar cane bagasse and rice straw feedstocks are used and converted into SGBs in SGBRs.

The first TGBR demonstration plant in the world was commissioned in Oulu, Finland, by Chempolis Oy. As far as is known, the world's first TGBR producing paper fiber, biofuel, and biochemicals from nonwood and nonfood materials was launched in Finland. TGBRs start with a mix of biomass feedstocks (agricultural or forest biomass) and produce a multiplicity of various products, such as ethanol for fuels, chemicals, and plastics, by applying a mix of different (both small- and

Table 7.6 Classification of biorefineries based on their generation technologies

Generation	Feedstocks	Examples
First	Sugar, starch, vegetable oils, animal fats	Bioalcohols, vegetable oil, biodiesel, biosyngas, biogas
Second	Non food crops, Wheat straw, Corn, Wood, Solid waste, Energy crop	Bioalcohols, bio-oil, bio-DMF, bio-hydrogen, bio-Fischer–Tropsch diesel
Third	Algae	Vegetable oil, biodiesel, jet fuel
Fourth	Vegetable oil, biodiesel	Biogasoline

large-scale) technologies such as extraction, separation, and thermochemical or biochemical conversion. However, large integrated TGBRs are not expected to become fully established until around 2020. Increasing quantities of agricultural residues will be needed to make paper in the future, as insufficient wood is available locally in the world's growing paper markets, forest resources are declining, and growing environmental pressures are being put on the use of wood. Vegetable oil is used and converted into biogasoline in fourth-generation biorefineries.

Biorefineries can also be classified based on their conversion routes: biosyngas-based biorefineries, pyrolysis-based biorefineries, hydrothermal-upgrading-based biorefineries, fermentation-based biorefineries, and oil-plant-based biorefineries. Table 7.7 shows the classification of biorefineries based on their conversion routes. Biosyngas is a multifunctional intermediate for the production of materials, chemicals, transportation fuels, power, and heat from biomass.

Table 7.7 Classification of biorefineries based on their conversion routes

Biorefinery	Products
Biosyngas-based	Syngas, hydrogen, methanol, dimethyl ether, FT diesel
Pyrolysis-based	Bio-oil, diesel fuel, chemicals, oxygenates, hydrogen
Hydrothermal-upgrading-based	C_xH_x, diesel fuel, chemicals
Fermentation-based	Bioethanol
Oil-plant-based	Biodiesel, diesel fuel, gasoline

7.5 Refining of Upgraded Products

A biorefinery system starts with the contract harvesting of whole crops (grain and straw), which are then stored and fractionated (including drying as necessary) into products and byproduct for sale. A biorefinery is a factory that processes crops, such as wheat, barley, and oilseed rape, to produce various refined specialized fractions, such as flour, gluten, starch, oil, straw chips, etc. The concept of a biorefinery, compared with, for example, a flour mill, is that the use and value of all the fractions into which the input can be separated is maximized (Audsley and Annetts 2003).

The analysis of a biorefinery system can be considered in three parts. The first is the effect on the farm of selling products to a biorefinery, on the assumption that the biorefinery contracts to harvest the crop using a wholecrop forage harvester. The second part is the impact of the type of biorefinery system on the profitability of the processing required to produce the various products. The third part is the transport of crop to the biorefinery, which is a function of the distribution of farms around the biorefinery location (Audsley and Annetts 2003).

As biomass hydrolysis and sugar fermentation technologies approach commercial viability, advancements in product recovery technologies will be required. For cases in which fermentation products are more volatile than water, recovery by distillation is often the technology of choice. Distillation technologies that will allow the economic recovery of dilute volatile products from streams containing a variety of impurities have been developed and commercially demonstrated. A distillation system separates the bioethanol from water in the liquid mixture.

The first step is to recover the bioethanol in a distillation or beer column, where most of the water remains with the solids part. The product (37% bioethanol) is then concentrated in a rectifying column to a concentration just below the azeotrope (95%). The remaining bottom product is fed to the stripping column to remove additional water, with the bioethanol distillate from stripping being recombined with the feed to the rectifier. The recovery of bioethanol in the distillation columns in the plant is fixed at 99.6% to reduce bioethanol losses.

After the first effect, solids are separated using a centrifuge and dried in a rotary dryer. A portion (25%) of the centrifuge effluent is recycled to fermentation and the rest is sent to the second and third evaporator effects. Most of the evaporator condensate is returned to the process as fairly clean condensate (a small portion, 10%, is split off to wastewater treatment to prevent buildup of low-boiling-point compounds) and the concentrated syrup contains 15 to 20% by weight total solids.

One of the advantages of alkane production from biomass by aqueous-phase dehydration/hydrogenation is that the alkanes spontaneously separate from the aqueous feed solution, whereas ethanol produced during fermentation processes must be removed from water by an energy-intensive distillation step.

Biomass-derived oxygenates can be converted into hydrogen and alkanes (ranging from C_1 to C_{15}) via aqueous-phase processing (Audsley and Annetts 2003). These aqueous-phase processes could be used in an integrated biorefinery to produce a range of fuels, as shown in Figure 7.5. The first step in the biorefining process is conversion of biomass into an aqueous sugar solution. Production of hydrogen for biorefining processes is accomplished by aqueous-phase reforming. The biorefinery can also produce light alkanes ranging from C_1 to C_6 by aqueous-phase dehydration/hydrogenation (Audsley and Annetts 2003). The light alkanes could be used as synthetic natural gas, liquefied petroleum gas, and a light naptha stream. Aqueous-phase processing can also produce larger alkanes ranging from C_7 to C_{15} by combining the dehydration/hydrogenation reactions with an aldol condensation step prior to the aqueous-phase dehydration/hydrogenation step (Huber *et al.* 2005).

Biomass has been traditionally converted into liquid fuels by either (a) fermentation or (b) pyrolysis methods. Modern improvements to these classical processes are many in number but do not essentially change the type of product resulting from these two vastly different sets of reaction conditions. While ethanol production by fermentation has become more efficient, it is still limited to a 67% yield due to the loss of one third (1/3) of the available carbon as carbon dioxide gas. Pyrolytic reactions also lose carbon as gases and char but may achieve about 80% carbon conversion. While most thermochemical processes usually require nearly dry feedstock, the hydrothermal upgrading (HTU) process requires a 3:1 ratio of water to biomass. However, HTU produces only 50% biocrude, which still contains 10 to 15% oxygen. Obviously, there remains a need for a variety of fuels from many sources, especially conventional liquid fuels for transportation purposes. To resolve this fuel problem

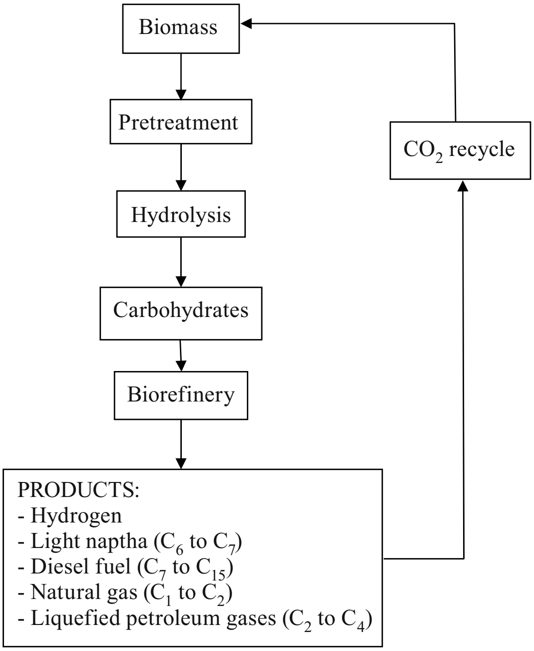


Figure 7.5 An integrated biorefinery for conversion of carbohydrates into fuels by aqueous-phase processing

and to use a renewable resource, a strategy was selected to prepare valuable liquid hydrocarbons from biomass by a new chemical process.

Glycerol can be converted into higher-value products. The products are 1,3-propanediol, 1,2-propanediol, dihydroxyacetones, hydrogen, polyglycerols, succinic acid, and polyesters. The main glycerol-based oxygenates are 1,3-propanediol, 1,2-propanediol, propanol, glycerol tertbutyl ethers, ethylene glycol, and propylene glycol. Glycerol has been pyrolyzed for the production of clean fuels such as H_2 or a feedstock such as syngas for additional transportation fuel via FTS.The conversion of glycerol to H_2 and CO takes place according to the following stoichiometric equation:

$$C_3O_3H_8 \rightarrow 3CO + 4H_2 \tag{7.1}$$

The stoichiometry for conversion of glycerol into liquid alkanes, by the formation of synthesis gas coupled with FTS, is shown in Equation 7.2:

$$25C_3O_3H_8 \rightarrow 7C_8H_{18} + 19CO_2 + 37H_2O \tag{7.2}$$

This overall reaction to produce liquid fuels from glycerol is slightly exothermic and the yield of liquid alkanes is 40% at 1.7 MPa pressure.

It is possible to produce light alkanes by aqueous-phase reforming of biomass-derived oxygenates such as sorbitol, which can be obtained from glucose by hydrogenation (Huber *et al.* 2005; Metzger 2006). The production of alkanes from aqueous carbohydrate solutions would be advantageous because of the easy separation of the alkanes from water. Much hydrogen is needed to reduce biomass-derived oxygenates to alkanes as shown in Equation 7.3:

$$C_6H_{14}O_6 + 6H_2 \rightarrow C_6H_{14} + 6H_2O \qquad (7.3)$$

Production of ethanol (bioethanol) from biomass is one way to reduce both the consumption of crude oil and environmental pollution. Ethanol from lignocellulosic biomass has the potential to contribute substantially to bioethanol for transportation. In the process evaluated, prehydrolysis with dilute sulfuric acid is employed to hydrolyze hemicellulose and make the cellulose more accessible to hydrolysis by enzymes. Residual biomass from hydrolysis and extraction of carbohydrates can be burned in a power plant to generate electricity and process steam. Figure 7.6 shows a flow diagram of pretreatment for fermentation of ethanol production from sugar crops and lignocellulosic feedstocks.

Carbohydrates (hemicelluloses and cellulose) in plant materials can be converted into sugars by hydrolysis. Fermentation is an anaerobic biological process in which sugars are converted into alcohol by the action of microorganisms, usually yeast. The resulting alcohol is bioethanol. The value of any particular type of biomass as feedstock for fermentation depends on the ease with which it can be converted into sugars. Bioethanol is a petrol additive/substitute. Bioethanol and the biorefinery concept are closely linked. It is possible that wood, straw, and even household wastes may be economically converted into bioethanol. In 2004, 3.4 billion gal. of fuel

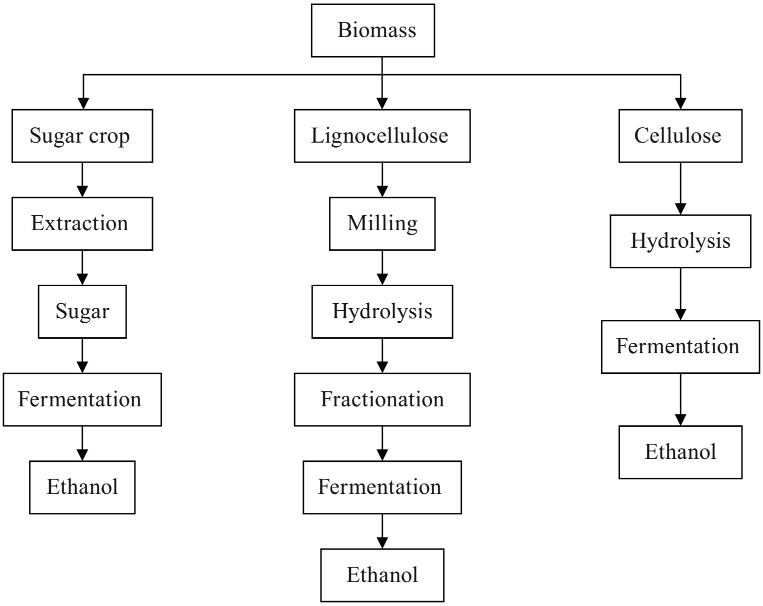


Figure 7.6 Pretreatment for fermentation of ethanol production from sugar crops and lignocellulosics

ethanol were produced from over 10% of the corn crop. Ethanol demand is expected to more than double in the next 10 years. For the supply to be available to meet this demand, new technologies must be moved from the laboratory to commercial reality. World ethanol production is about 60% from sugar-crop feedstock.

The corn-starch-to-fuel-ethanol industry has been developed over the past 30 years by bioethanol researchers. Most bioethanol researchers focus on the challenge of producing bioethanol from lignocellulosic biomass instead of from corn starch. To this end, researchers have already developed effective technology to thermochemically pretreat biomass, to hydrolyze hemicellulose to break it down into its component sugars and open up the cellulose to treatment, to enzymatically hydrolyze cellulose to break it down into sugars, and to ferment both 5-carbon sugars from hemicellulose and 6-carbon sugars from cellulose.

Cellulose is a remarkable pure organic polymer, consisting solely of units of anhydroglucose held together in a giant straight-chain molecule. Cellulose must be hydrolyzed to glucose before fermentation into ethanol. Conversion efficiencies of cellulose to glucose may depend on the extent of chemical and mechanical pretreatments to structurally and chemically alter the pulp and paper mill wastes. The method of pulping, the type of wood, and the use of recycled pulp and paper products also could influence the accessibility of cellulose to cellulase enzymes.

Cellulose fraction of the structural components is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis. Hemicelluloses (arabinoglycuronoxylan and galactoglucomammans) are related to plant gums in composition and occur in much shorter molecule chains than cellulose. The hemicelluloses, which are present in deciduous woods chiefly as pentosans and in coniferous woods almost entirely as hexosanes, undergo thermal decomposition very readily. Hemicelluloses are derived mainly from chains of pentose sugars and act as the cement material holding together the cellulose micells and fiber. Hemicelluloses are largely soluble in alkali and as such are more easily hydrolyzed.

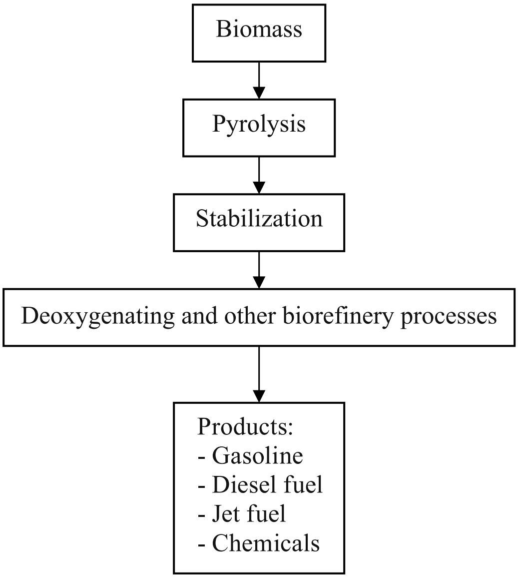
7.6 Opportunities for Refining Pyrolysis Products

Biorefinery refers to the conversion of biomass feedstock into value-added chemicals and fuels with minimal waste and emissions. Some current aspects of biorefinery research and development since the early 1990s are presented, revealing that integrated processes, biomass upgrading technology, and biorefinery technology have become objects of research and development. Many of the currently used biorenewable-based industry products are the results of direct physical, catalytic, or chemical treatment and processing of biomass feedstocks.

The primary objective refining of pyrolysis products is to obtain valuable fuels like gasoline, diesel and jet fuel, and chemicals from biomass. Figure 7.7 shows the products from biomass by pyrolysis-based refining.

In vacuum pyrolysis, biomass is heated in a vacuum in order to decrease the boiling point and avoid adverse chemical reactions. In flash vacuum thermolysis

Figure 7.7 Products from biomass by pyrolysis-based refinery



(FVT), the residence time of the substrate at the working temperature is limited as much as possible, again in order to minimize secondary reactions.

Vacuum pyrolysis is the thermal degradation of a feedstock in the absence of oxygen and under low pressure to produce a bio-oil and char as main products, together with water and noncondensable gases. Both the bio-oil and char have a high energy content and may be used as fuels. An incredible number of chemical compounds are also found in the bio-oil, and these compounds can be extracted and sold as high-value chemicals.

Vacuum pyrolysis is a relatively new variant of pyrolysis with many recycling applications. During vacuum pyrolysis of biomass, the biorenewable feedstock is thermally decomposed under reduced pressure. The quick removal of the vapors reduces the residence times of the macromolecules and hence minimizes secondary decomposition reactions such as cracking, repolymerization, and recondensation, which occur during atmospheric pyrolysis. Temperatures between 675 K and 775 K and pressures of about 0.15 atm are typically used. Table 7.8 compares pyrolysis and gasification processes.

Bio-oil contains the thermally cracked products of the original cellulose, hemicelluloses, and lignin fractions present in biomass. It also contains a high percentage of water, often as high as 30%. The total oil is often homogeneous after quenching but can easily be separated into two fractions, a water-soluble fraction and a heavier pyrolytic lignin fraction. The addition of more water allows the pyrolytic lignin fraction to be isolated, and the majority of it consists of the same phenolic polymer as lignin but with smaller-molecular-weight fragments. Bio-oils are composed of a range of cyclopentanone, methoxyphenol, acetic acid, methanol, acetone, furfural, phenol, formic acid, levoglucosan, guaioco,l and their alkylated phenol derivatives.

Table 7.8 Comparison of pyrolysis and gasification processes

Process	Conditions	Products, wt%		
		Liquid	Char	Gas
Fast pyrolysis	Moderate temperature (700–800 K) Short hot vapor residence time (< 2 s)	70–77	10–14	11–15
Slow pyrolysis	Low-moderate temperature (600–725 K) Long residence time	27–33	33–38	33–38
Vacuum pyrolysis	Moderate temperature (675–775 K) Low pressure (< 0.15 atm)	74–80	8–12	9–14
Gasification	High temperature ($>$ 1,075 K) Long residence time	4–6	8–12	82–88

Pyrolytic lignin is a better feedstock for liquid fuel production than the water-soluble fraction because of its lower oxygen content, and therefore the study focused on evaluating it as a potential feedstock for the production of highly aromatic gasoline (Demirbas 2000).

The pyrolysis of biomass is a thermal treatment that results in the production of charcoal, liquid, and gaseous products. Among the liquid products, methanol is one of the most valuable. The liquid fraction of the pyrolysis products consists of two phases: an aqueous phase containing a wide variety of organooxygen compounds of low molecular weight and a nonaqueous phase containing insoluble organics of high molecular weight. This phase is called tar and is the product of greatest interest. The ratios of acetic acid, methanol, and acetone of the aqueous phase are higher than those of the nonaqueous phase.

The bio-oil formed at 725 K contain high concentrations of compounds such as acetic acid, 1-hydroxy-2-butanone, 1-hydroxy-2-propanone, methanol, 2,6-dimethoxyphenol, 4-methyl-2,6-dimetoxyphenol, 2-cyclopenten-1-one, etc. A significant characteristic of bio-oils is the high percentage of alkylated compounds, especially methyl derivatives (Demirbas 2007).

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