
RENEWABLE MATERIALS

8.1 INTRODUCTION

Resources can be classified as finite (with limited existence) or infinite (endless supply); or as renewable (capable of being replaced naturally and replenished on a reasonable timescale), nonrenewable (only capable of being replenished at a very slow rate), and perpetual (such as sunlight and wind). Nonrenewable resources (such as petroleum, coal, and minerals) are generally extracted from the earth. On the other hand, renewable resources (such as biomass) are grown.

One of the central tenants of green chemistry is that raw materials should be derived from renewable resources whenever possible. Effectively the seventh principle of green chemistry states that “a raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable” [1, p. 45]. Petrochemical resources are clearly limited, although there remains discussion as to how long these nonrenewable resources can last. Thus, for processes to be truly sustainable, raw materials must be derived from plants or microbial sources and,

because fossil resources can be used in the production of renewable materials, should be produced with noninvasive chemical processing.

This chapter explores the sources of renewable feedstocks, in particular, carbohydrates, lignin, lipid oils, and proteins, followed by the production of chemicals from renewable resources, and finally some current applications of renewable materials.

8.2 RENEWABLE FEEDSTOCKS

8.2.1 Role of Biomass and Components

Biomass is often defined as “a renewable energy source, living or recently living biological material” such as wood, waste, and alcohol fuels [2]. Biomass is often associated with plant-based material but it also applies to both animal- and vegetable-derived material.

The chemical structure of biomass is comprised of a mixture of elements found in organic molecules, including carbon, oxygen, hydrogen, and nitrogen atoms, as well as other atoms such as alkali, alkaline earth, and heavy metals. But in general, biomass is a polymeric material without a regular structure, and thus there is no such thing as a biomass molecule.

According to the Biomass Energy Center in the United Kingdom, there are five categories of biomass materials including “virgin wood from forestry, arboricultural activities, or from wood processing; energy crops such as high yield crops grown specifically for energy applications; agricultural residues; food waste from food and drink manufacture, preparation and processing, and post-consumer waste; and industrial waste and co-products from manufacturing and industrial processes.” Common sources of biomass include wood materials, such as bark, sawdust, and mill scrap; agricultural wastes such as corn stalks and straw, manure from cattle, and waste from poultry; municipal waste such as paper and yard clippings; and energy crops such as corn (starch), switchgrass, soybean (oil), and alfalfa (pasture and hay crop) [3].

In order to evaluate the environmental impact of biomass, one needs to evaluate the carbon cycle of the process. Carbon from the atmosphere is converted into biological matter through photosynthesis. If the biomass is used to produce energy through combustion, the final carbon product is carbon dioxide, a significant greenhouse gas. However, the carbon originated from atmospheric CO_2 , and thus combustion merely returns the carbon back into the atmosphere and there should be no net gain in atmospheric CO_2 . However, if the biomass is not regenerated through new planting, this cycle is disturbed and biomass combustion and use can contribute to a larger extent to global warming. This happens in the case of deforestation and intense urbanization. In Figure 8.1, the full cycle is shown.

Figure 8.1 shows four steps in the complete carbon cycle.

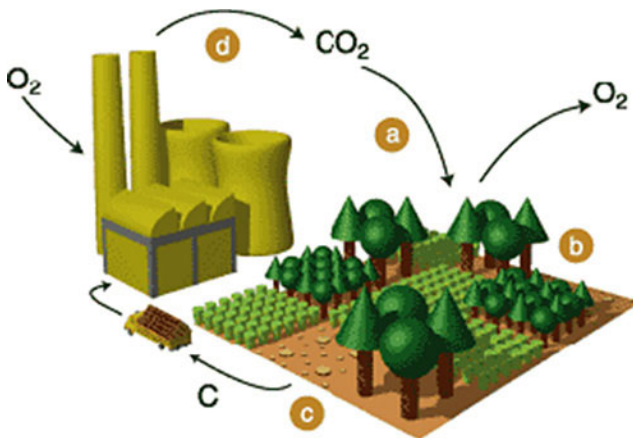


Figure 8.1. Absorption and emission of carbon dioxide through combustion of biomass [4]. (R. Mathews for IEA Bioenergy Task 38.)

- (a) Trees in the energy plantation grow, absorbing carbon dioxide from the atmosphere.
- (b) During photosynthesis, the trees store carbon in their woody tissue and oxygen is released back to the atmosphere.
- (c) The biomass is harvested and then transported from the plantation to the power plant. Unless the vehicle is fueled from bioderived materials, there is a net consumption of nonrenewable materials and a contribution to atmospheric CO₂.
- (d) The wood is burned in the power plant, generating carbon dioxide through the combustion of carbon stored in the woody tissue. The CO₂ is released back to the atmosphere in the exhaust gases.

Under perfect conditions, the absorption of CO₂ through plant growth would be perfectly balanced with the emission of CO₂ through combustion. However, the process of growing biomass is facilitated through the use of fertilizers and pesticides, and machinery is used to perform planting, harvesting, processing, and transport, consuming fossil resources. Thus, biomass is often referred to as “a low carbon fuel.”

Fossil fuels such as coal, oil, and gas are also derived from biological materials. However, the biological materials from which fossil fuels derive absorbed carbon dioxide from the atmosphere many millions of years ago. When their combustion products are released into the atmosphere, there is no process occurring at a comparable rate that consumes this additional CO₂. Unless they are captured and stored, the combustion of fossil resources contributes to increased levels of CO₂ in the atmosphere.

Biomass is a complex substance made up of many organic species combined into a heterogeneous polymeric material. Although the actual structure of biomass cannot be defined, portions of it can be related to the structure of known organic compounds. These structures include carbohydrates (cellulose and hemicelluloses, approximately

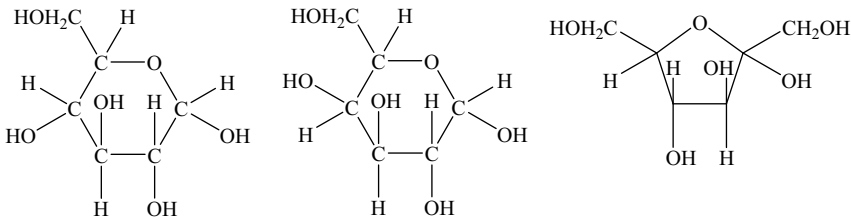


Figure 8.2. Basic carbohydrates of (a) glucose, (b) galactose, and (c) fructose.

75%, dry weight) followed by lignin, then fats and proteins, and small amounts of minerals, such as sodium, phosphorus, calcium, and iron.

8.2.1.1 Carbohydrates

Carbohydrates, or saccharides, make most of the organic matter on earth. They hold numerous roles such as the storage and transport of energy in living things (e.g., starch and glycogen) and are part of the structural framework of RNA (ribonucleic acid) and DNA (deoxyribonucleic acid) (e.g., ribose and deoxyribose, a component of DNA) and of plant cell walls and plant tissues (e.g., polysaccharides such as cellulose).

Carbohydrates are related to simple organic compounds, such as aldehydes and ketones with added hydroxyl groups. Monosaccharides, such as glucose (necessary “blood sugar” for cellular respiration), galactose (sugar found in milk and yogurts), and fructose (sugar found in honey), are the basic carbohydrates. They are structural isomers: they have identical molecular formulas $C_6H_{12}O_6$ but different structural formulas (Figure 8.2).

When monosaccharides are linked together, they form polysaccharides (or oligosaccharides) such as lactose, which is a disaccharide occurring naturally in mammalian milk. Polysaccharides, such as starch and cellulose, are an important class of biological polymers.

Starch, a polymer of glucose, is used as an energy storage polysaccharide in all green plants and is present in a lot of food sources for humans (breads, pastas, potatoes, rice, some cereals). There are two types of starch molecules: amylose and amylopectin (Figures 8.3 and 8.4).

“Animal starch,” also known as glycogen, is related to glucose in an analogous way as amylopectin is related to amylose; glycogen provides a convenient way for animals to store energy as it gets metabolized quickly in active animals.

There is around 60 million tons of raw starch produced annually for food and nonfood uses. The major sources of starch include rice, wheat, potatoes, cassava (tapioca), and corn, which accounts for over 80% of the world production. Corn is used in the United States as a fermentation feedstock for bioethanol production, discussed later in this chapter. Starch is produced by steeping the raw material in hot water, which releases the starch from the binders also present in the biomass.

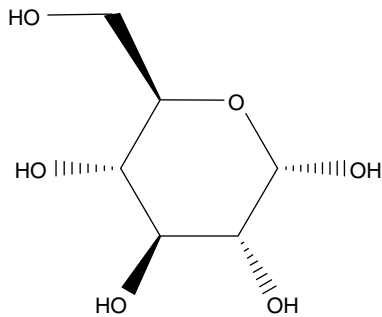


Figure 8.3. Structure of amylose.

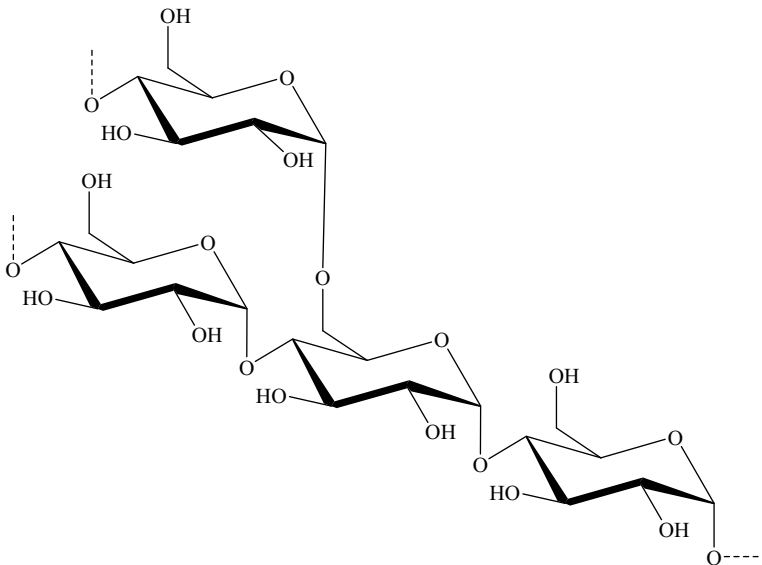


Figure 8.4. Structure of amylopectin.

The water is then evaporated, and the starch can be separated from the oil and other components released through the hot water treatment.

Cellulose is another important carbohydrate consisting of linked D-glucose units found in the primary cell wall of green plants and other organisms such as algae and water molds.

Cellulose, a long-chain polymer with the molecular formula $(C_6H_{10}O_5)_n$, is the most common organic compound on earth (Figure 8.5). Commercial cellulose is mainly obtained from wood pulp and cotton. The list of commercial products made from cellulose is extensive, including primarily paper, cardboard, and cardstock, and textiles made from cotton, linen, and other plant fibers. Cellulose can also be converted into cellophane, a thin transparent film, or used in the manufacture of nitrocellulose

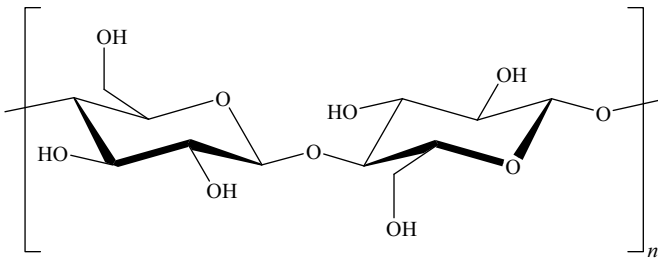


Figure 8.5. Structure of cellulose.

(cellulose nitrate) employed historically in smokeless gunpowder. Cellulose esters such as cellulose acetate are used in a wide range of products including cigarette filters, films, and filtration membranes in the pharmaceutical sector. Alkyls of cellulose esters are also used in the cosmetic and pharmaceutical industries.

Cellulose is generally produced through wood pulping, a process not too dissimilar from the steeping process used to produce starch. In this case, high temperatures are required to break down the lignin that binds the cellulose fibers together. Additional oxidizers may also be added to enhance the process. Once the lignin is removed, the cellulose fibers can be recovered. Cellulose can also be recovered from recycled paper using a similar process. Because of the nature of the secondary processing, recycled cellulose may be used as a material for building insulation, which is environmentally preferable over the often petrochemical-based insulation types including foam and fiberglass.

8.2.1.2 Lignin

Following carbohydrates (starch and cellulose), the next most abundant species in biomass is the biopolymer, lignin, found in the secondary cell walls of plants and some algae. Lignin is a noncarbohydrate macromolecule with a complex, highly aromatic and indeterminate primary structure. Its main function is to fill void spaces in the cell wall and therefore to provide mechanical strength as well as prevent enzymatic and chemical degradation of cellulose. Wood with high lignin content is durable and is consequently used in a lot of applications.

Lignin is present in high quantity in the wood pulp used to make paper, and its presence contributes to the yellowing of newsprint with age. In order to produce high quality bleached paper, lignin needs to be removed from the wood pulp as sulfonates, usually via the Kraft process known as sulfate pulping. Sulfonates are the conjugate bases of sulfonic acids and are anionic species of the type RSO_3^- .

After removal of the lignin, it can be dewatered and then burned as a fuel, providing more energy than cellulose and enough energy to run a typical paper mill. The sulfonates of lignin can be used as dispersants in paints, in cement applications, as additives in pesticides and cleaning agents, and as environmentally conscious dust suppression agents.

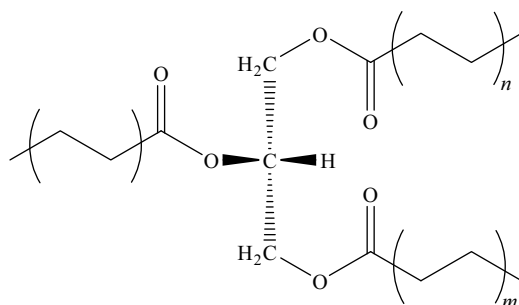


Figure 8.6. General structure of a triglyceride molecule (m , n , and p are whole numbers).

8.2.1.3 Oils/Fats

The most efficient oil-producing crops are tropical crops such as coconut and palm, followed by sunflower and soybean. Other fruit and nut oils are also extracted for food use but the need for high content of fatty acids or fatty acid derivatives tends to limit their industrial use. Vegetable oils, animal fats, or recycled greases are used as feedstocks for the production of biodiesel, with soybean oil as the most commonly used oil in the United States.

The most important component of plant-derived oils is triglycerides or triacylglycerides, which constitute 93–98% by weight of the oil. Each plant or vegetable species will have a different mixture of triglyceride molecules. A triglyceride molecule contains a molecule of glycerol commonly called glycerin or glycerine combined with three fatty acids (Figure 8.6).

The carbon chains of the fatty acids in the natural fats vary in length. For example, in cocoa butter, three fatty acids—palmitic, oleic, and stearic acids—have a low melting point of about 34 – 38 °C. This explains why chocolate is a solid at room temperature but melts once in the mouth.

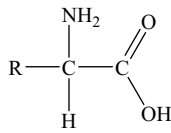
Vegetable-based oils find many applications in industry such as for lubricants (increased biodegradability of vegetable oils is an advantage when used in marine or forest environments), for detergent, soap, and cleaning formulations, for solvents, and for plastics manufacturing.

8.2.1.4 Proteins and Amino Acids

Seeds of legumes are important sources of protein and are commonly used commercially as animal feed supplements or may be used for cosmetic purposes. Unfortunately, extracting proteins in high quantities without modifying their structural and chemical properties is a challenge.

The proteins in plants are comprised of amino acids, small molecules that contain both amine and acidic groups (Figure 8.7).

The length of the chain and any additional functionality in the chain provide the amino acid with its specific chemical properties and determine what types of further



Typical structure of an amino acid with different R groups such as

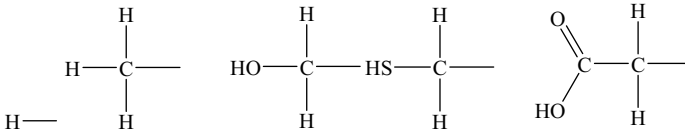


Figure 8.7. Amino acids (in this order: glycine, alanine, serine, cysteine, and aspartate).

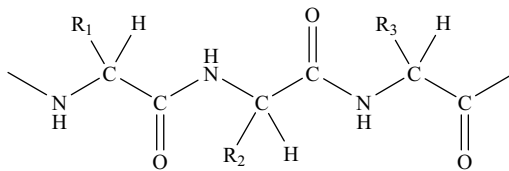


Figure 8.8. Primary structure of a protein (R_1 , R_2 , R_3 are alkyl groups).

processing might be appropriate. The protein is developed as the amino acids join together through peptide bonds (Figure 8.8).

The nature of the protein is then determined by the exact sequence of amino acids from which it is comprised.

8.2.2 Production of Chemicals from Renewable Resources

The chemical industry is heavily dependent on oil, which is the major feedstock for the production of chemicals, and a significant source of energy, particularly for vehicle applications. More than 90% of all organic compounds are derived from petroleum. However, the increased world demand for petroleum-based products and energy, as well as the finite reserve of crude oil, pose an enormous sustainability challenge. Combustion of fossil resources produces CO_2 , which leads to climate change. And there is no doubt that fossil resources are in limited supply. Thus, strategies based on renewable sources are warranted.

Biomass resources can be used directly as a fuel, generally through combustion. But to be able to derive a chemical industry based on renewable resources, it is necessary to convert the structures within the biomass into useful chemicals that can replace chemicals currently produced from petroleum-derived compounds. This remains a significant challenge and the basis of a great deal of ongoing research.

Recognizing the efficiencies of the petroleum refinery in producing a large variety of products simultaneously, conventional thought is that the most effective plan for conversion of bioresources will be through a biorefinery process. In the petrorefinery process based on a “build-up” approach, feedstocks such as crude oil

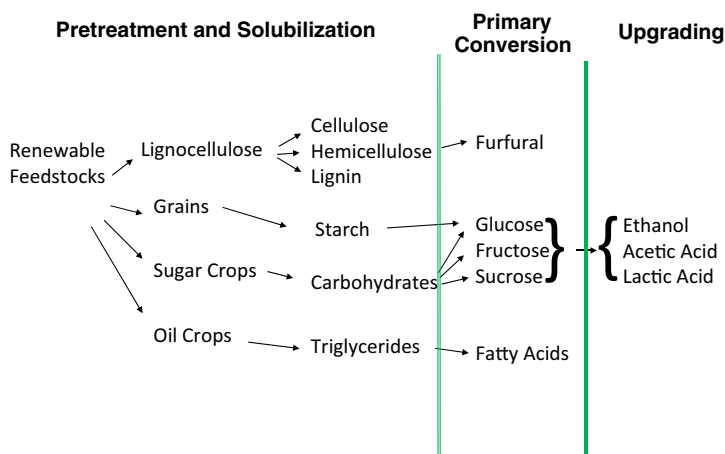


Figure 8.9. Conversion of renewable feedstocks to fuels and chemicals.

and natural gas are converted into products such as energy (fuels), specialty and commodity chemicals, and materials (plastics). In the integrated biorefinery approach the feedstock is biomass (trees, crops, plants, grass, waste, etc.), which is changed into energy, chemicals, and materials plus food and feed. However, one crucial difference between the two processes is that the plant materials need to be broken down into simpler building block molecules first, before they can be converted into more complex products. Thus, a typical biorefinery might involve the steps shown in Figure 8.9 as the basis by which fuels and chemicals can be produced from renewable resources.

In general, the reactions needed for the conversion process required for biomass resources are different from those associated with fossil resources. Fossil fuels contain primarily carbon and hydrogen, and the conversion processes are based on oxidation of the derived molecules. Most of the species are not soluble in water and remain relatively stable at elevated temperatures. Bio-derived molecules are very different. They often contain significant quantities of oxygen and must be reduced to give the desired functionalities. They decompose at elevated temperatures and are soluble in water. So while the same range of chemistry is available for the processing of bio-derived molecules as would be the case for fossil resources, such processes are not usually economically practical, and new processing techniques are required.

There are two primary mechanisms available for conversion of biomass into useful chemicals, as shown in Figure 8.10 [5]. One is through thermochemical treatment, which essentially takes advantage of traditional chemical processing techniques to convert the biomass into a material that can be accommodated through conventional technologies used for processing of fossil resources. A second route focuses on biological processes using enzymatic methods and processing in water, usually at relatively low temperature, but often at rates significantly slower than traditional chemical processes. Either route can provide a viable pathway to desired chemical products and should be evaluated on a life cycle basis to determine the

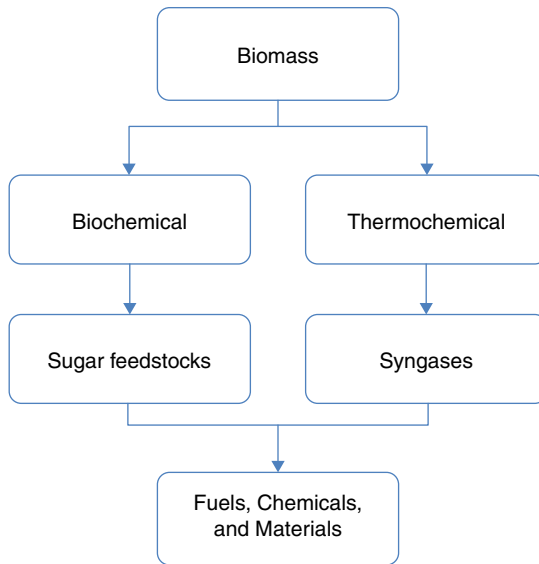


Figure 8.10. The biorefinery concept.

sustainability of the process route. Eventually, the biorefinery will need to take advantage of both platforms through integrated processes that also allow for interchange of materials between the two routes and the use of thermal energy produced as a part of the processing.

8.2.2.1 Conversion of Biomass Through Thermochemical Processes

Gasification is a thermochemical technique for converting biomass into a product conventionally called synthesis gas (or syngas), essentially CO and H₂. The process is conducted at elevated temperatures (typically greater than 700 °C), with only a small amount (or no) oxygen present. By carefully controlling the oxygen content in the feed gas, the composition of the product can be controlled. Typically, methane and CO₂ are also produced during gasification, as well as some liquid oils and solid char. Oils produced during gasification can be separately recovered and recycled for further gasification or converted to other materials. However, the char is essentially a pure carbon waste product that has very limited commercial value and is thus an undesirable side product of the reaction. By adjusting the process conditions, one can tune the composition of the products to achieve a desirable gas mixture that can be used for later processes. A typical thermochemical process is pictured in Figure 8.11.

Syngas is a platform product that allows biomass to be converted to traditional chemical products, most typically through a process known as Fischer–Tropsch (F-T). The F-T technology is not new and has been employed for the conversion of

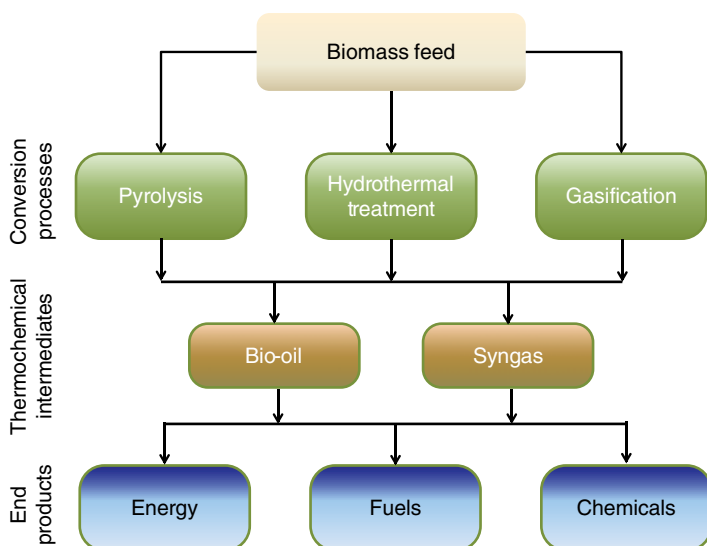


Figure 8.11. A typical thermochemical process and its products.

coal and natural gas to chemicals since World War I, when the Germans used this process for the production of gasoline. More recently, South Africa relied on this technology to produce hydrocarbon products from coal throughout the apartheid era. In all of these cases, the economics of the process relative to other choices for obtaining the desired product drove the development of the technology. The current interest for conversion of biomass to traditional hydrocarbon products represents a similar economic opportunity, since the efficiency of other conversion processes has not yet been demonstrated on a large scale.

The first step of the gasification process is through combustion, in which the carbon and hydrogen are converted to CO_2 and water. Because the reactions are exothermic, temperatures in excess of 1000°C can be achieved, depending on how much residual water is retained within the fuel. The extent of combustion is controlled by the amount of oxygen present in the fuel. After all of the oxygen is consumed, a series of reduction reactions occur that convert the CO_2 to CO , either by disproportionation with residual carbon



or through reaction of residual carbon with water

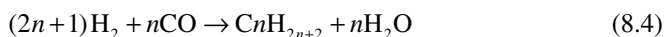


or through the water gas shift reaction



When the reaction is carried out using air as the source of oxygen, a product is formed that is roughly equal parts of syngas, containing roughly equal portions of CO, H₂, and CO₂, and the remainder being diluent nitrogen. Pure oxygen can be used in place of air, which substantially increases the energy content of the syngas, but at increased cost required for the separation of oxygen from air.

Once the syngas is produced, the Fischer–Tropsch process can be used to produce primarily alkanes, through what is essentially a polymerization reaction



where n is a positive integer. A range of alkanes are produced, generally following the Anderson–Shultz–Flory distribution, described as

$$W_n / n = (1 - \alpha)^2 \alpha^{n-1} \quad (8.5)$$

where W_n is the weight fraction of hydrocarbon molecules containing n carbon atoms and α is the chain growth probability. The selection of the catalyst and process conditions determines the value of α , which in turn determines the relative fraction of small or large hydrocarbon molecules in the product. The reaction also produces alkenes and alcohols as side products.

Two different catalysts can be used, depending on the desired products. A highly active cobalt-based catalyst can be used for low-temperature conversion at 150–200 °C, whereas an iron-based material is used at elevated temperatures of 300–350 °C. During the low-temperature synthesis, the catalyst is dispersed in a liquid slurry, whereas the high-temperature process is normally carried out in the vapor phase. The high-temperature process yields a greater preponderance of oxygenates, whereas the low-temperature process yields a product that more closely mimics traditional diesel fuel. The low-temperature F-T process is considered the more efficient, because the reactor cost is less, lower catalyst loading is possible, higher conversions can be achieved, and the catalyst has greater longevity. Regardless of the F-T process used, the product must then be upgraded to create a viable alternative fuel, or further refined to create the desired chemical product.

8.2.2.2 Conversion of Glucose Through Chemical Processes

Naturally occurring sugars such as glucose and fructose are gaining popularity as one of the most used feedstocks for the production of many commodity materials. Glucose, the building block of cellulose, can be converted to 5-hydroxymethylfurfural (HMF), a “platform chemical” in the production of compounds currently derived from petroleum such as solvents, fuels, and monomers [6]. HMF is produced through dehydration of glucose, by conversion to fructose through isomerization in the presence of alkali, and then through dehydration in the presence of an acid catalyst, or with titanium dioxide TiO₂. In either case, the reaction is carried out in hot compressed water at about 473 °C (Figure 8.12).

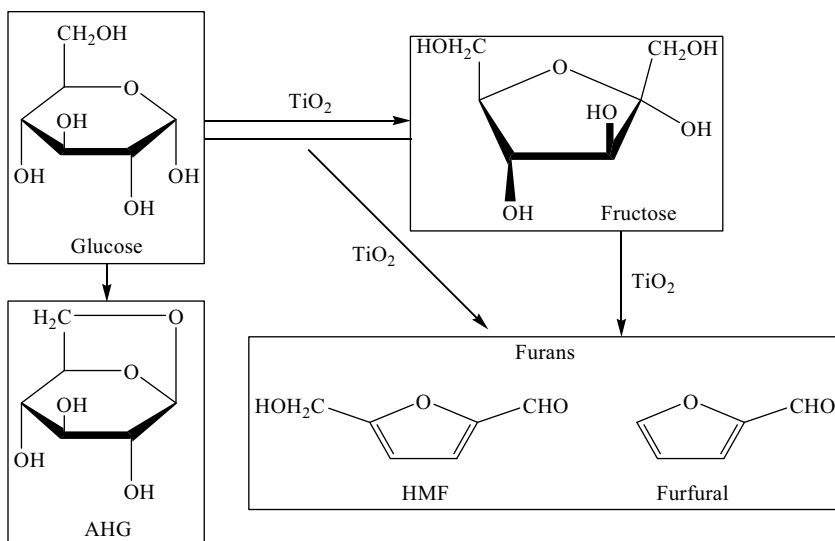


Figure 8.12. Conversion of glucose to HMF.

HMF can then be converted to 2,5-diformylfuran through oxidation, from which it can be used as a monomer for polymer formation, or as an intermediate for pharmaceuticals and other chemical intermediates [7].

Numerous chemicals can also be derived through fermentation of glucose and sucrose. A wide range of microorganisms can be used to break down the sugars into smaller molecules, under various reaction conditions and with variable efficiencies. However, these reactions are generally not particularly selective, as the microorganism is supporting the reaction in order to produce energy for its own sustenance. Thus, the products of the reaction are often dilute and in low yield, and substantial separation and purification steps are required to achieve a useful chemical product. Regardless, the ability to make chemicals directly from biomass continues to increase in interest, as the costs and environmental impacts of consuming nonrenewable resources become more definite.

Fermentation of glucose yields several primary acid products, as shown in Figure 8.13 [8]. Each of these products can then be converted to other useful chemicals.

Approximately 350,000 tons/year of lactic acid is produced from glucose. The lactic acid can be converted through traditional chemical routes to yield well-known chemical products such as acrylic acid and propanediol. Lactic acid is also the building block for polylactic acid (PLA), a biodegradable polymer that has the potential to replace several existing polymer products in high use (Figure 8.14) [9].

The other primary fermentation products of glucose are equally valuable as raw materials for chemical production. Succinic acid can be converted through hydrogenation to butanediol, and then through dehydration to tetrahydrofuran. 3-Hydroxypropionic acid (3HPA) has bifunctionality that allows for reduction of the acid group to alcohol, esters, and amides, dehydration of the alcohol function to

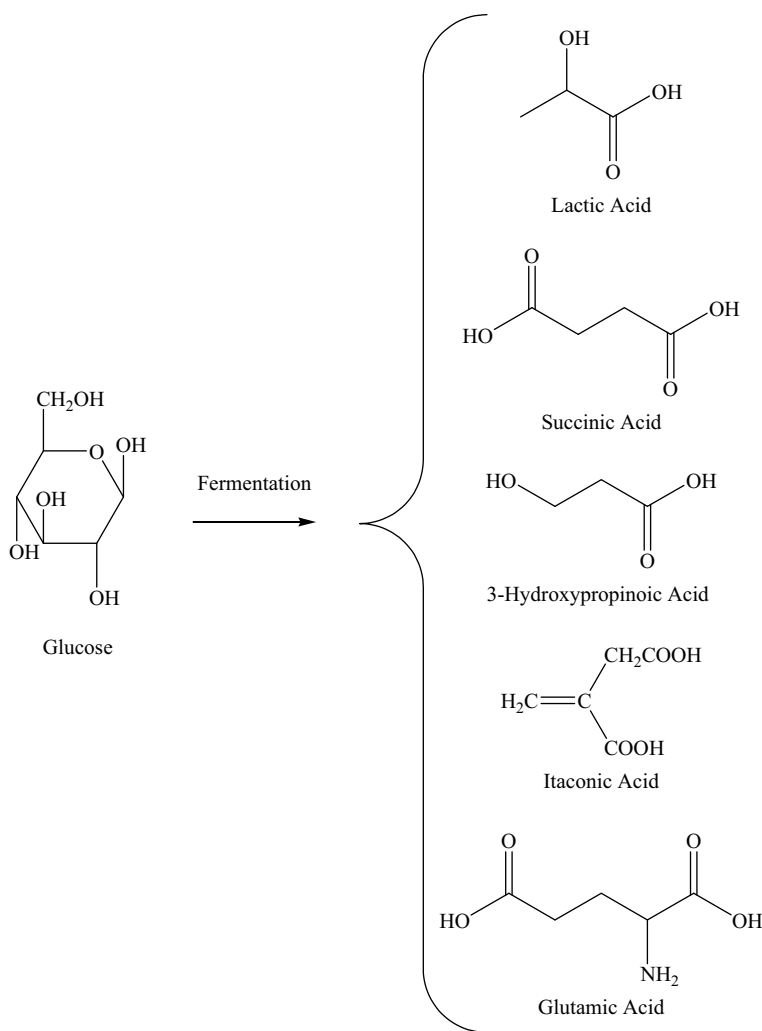


Figure 8.13. Products of fermentation of glucose.

produce unsaturated compounds, polymerization to polyesters and oligomers, and cyclization to propiolactone and lactides.

While it is clear that conversion of glucose into chemical building blocks through fermentation is a valuable route to chemicals production, glucose can be a valuable raw material in its own right. One of the important commercial synthetic routes to the production of vitamin C, ascorbic acid, is based on glucose [10]. Several process improvements have been made since the basic synthetic route developed in the 1930s. The bacterial process now uses *Acetobacter suboxydans*, a bacterium more resistant to the nickel catalyst used in the hydrogenation step. This nickel catalyst is the subject

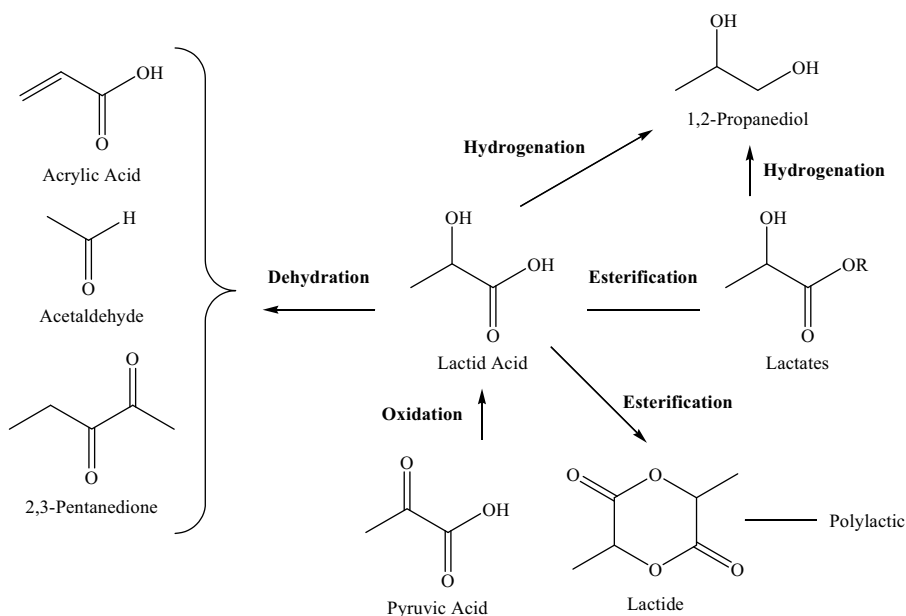


Figure 8.14. Products derived from lactic acid.

of environmental concern due to its toxicity. More recently, a one-step synthesis of L-ascorbic acid from D-glucose was presented [10]. According to the U.S. Patent #5998634 this mixture is “catalytically oxidized in aqueous solution by hypochlorous acid. L-Ascorbic acid can be separated from the aqueous solution, and the unconverted reactants recycled for greater conversion.”

Glucose is also an excellent replacement for benzene, a known carcinogen, in the synthesis of many aromatic compounds such as hydroquinone $[\text{C}_6\text{H}_4(\text{OH})_2]$, catechol $[\text{C}_6\text{H}_4(\text{OH})_2]$, and adipic acid $[(\text{CH}_2)_4(\text{COOH})_2]$ represented in Figure 8.15 [1, p. 94].

The use of glucose instead of benzene allows the substitution of organic solvents by water. The standard process for the production of adipic acid is based on the nitric acid oxidation of a cyclohexanol/cyclohexanone mixture derived from cyclohexane, which is in turn derived from benzene. Note that this process produces N_2O as a by-product of the reaction (Scheme 8.1).

Alternatively, adipic acid can be produced through biological conversion of benzoic acid or other aromatics derived from glucose to *cis*-muconic acid, which can then be converted to adipic acid by hydrogenation. Life cycle analysis of these two processes shows that the biological route can reduce the CO_2 equivalent emissions from 17.4 to 14.0 ton CO_2 eq/ton adipic acid, even beyond the environmental benefits associated with the elimination of the use of benzene derived from fossil resources [11].

Another example of the direct use of a renewable chemical is the biocatalytic conversion of D-glucose into vanillin used as a flavoring agent in food and beverages [12]. The use of a recombinant *Escherichia coli* biocatalyst in fermentation offers many advantages over the synthetic vanillin manufacture based on the use of

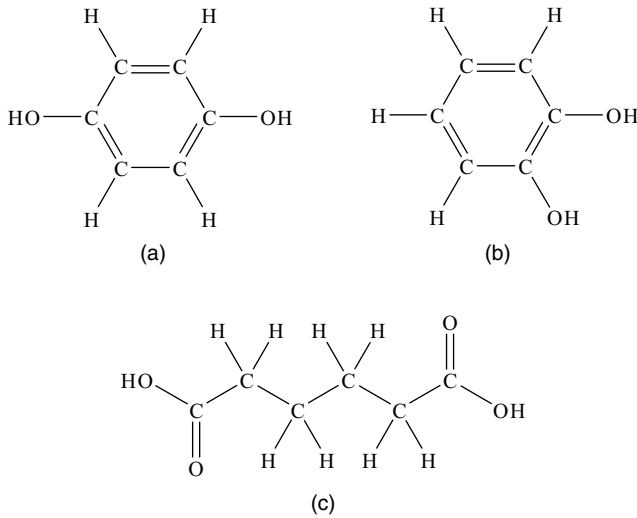
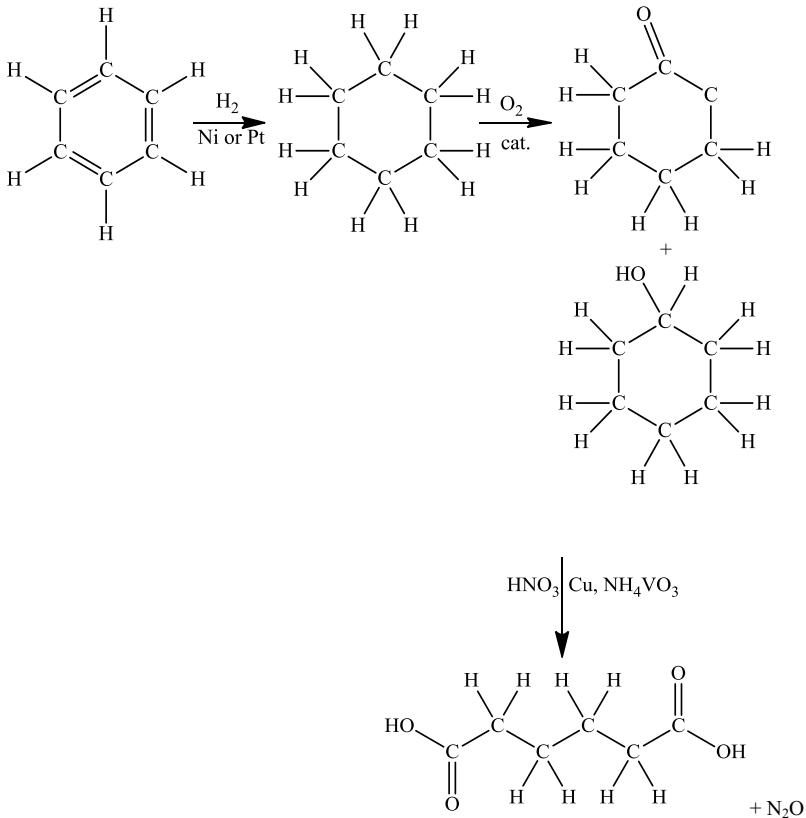


Figure 8.15. Structural formulas of (a) hydroquinone, (b) catechol, and (c) adipic acid.



Scheme 8.1 Conversion of benzene to adipic acid.

nonrenewable petroleum. The feedstock commonly used in the synthesis of vanillin is phenol derived from carcinogenic benzene; phenol gets eliminated and replaced by glucose derived from renewable starch.

8.3 APPLICATIONS OF RENEWABLE MATERIALS

8.3.1 The Case of Biodegradable Plastics

In almost every product we buy, there is some plastic! Packaging and containers is the largest market for plastics. They are cheap to produce, ensure excellent protection to the product, and last forever. Nevertheless, this third property is not ideal from an environmental point of view since traditional plastics are manufactured from nonrenewable and fossil-fuel-based resources such as oil, coal, and natural gas.

Designing for biodegradability is part of the intrinsic nature of green chemistry. The tenth principle of green chemistry states that “chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products” [1, p. 52].

A common definition of “biodegradable” is “capable of being broken down especially into innocuous products by the action of living things (microorganisms)” according to the Merriam–Webster online dictionary. The biodegradation of substances in the environment is helped by the action of bacteria, fungi, and protozoa. The goal of biodegradation is to reduce and, if possible, eliminate the toxicity of a substance by modifying it. Biodegradable plastics are typically derived from naturally occurring materials such as lactic acid and can be broken down by naturally occurring organisms. Highlight 8.1 provides options on what to do with plastic bottles.

Highlight 8.1 What Can We Do with Plastic Bottles?

Even if recycling plastic bottles seems very common these days, only 23% of water plastic bottles that Americans use are recycled. This leads to 38 billion water bottles ending up in landfills, where they can remain in their manufactured form for 1000 years before they are fully decomposed. When water bottles are burned in an incinerator, they can release toxic fumes and other gases involved in the destruction of the ozone layer.

Recycled water bottles made of polyethylene terephthalate (PET) have found many uses, especially in the clothing industry. Some of the companies using recycled PET fabric include Billabong’s Eco-Supreme Suede, Wellman Inc.’s Eco-fi, and Reware’s Rewoven.

The most-often recycled plastic is polyethylene, designated with the number 2 on bottles, which can be used in applications such as roadside curbs, trash receptacles, and benches.

However, the bottle’s cap is not made of the same type of polymer as the bottle itself and therefore needs to be separated from the PET bottle during the recycling process.

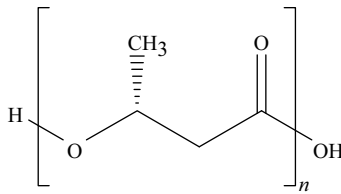


Figure 8.16 . Structure of poly-3-hydroxybutyrate (PHB).

Polyhydroxyalkanoates or PHA are thermoplastics produced by bacterial fermentation of sugars or lipids. Maurice Lemoigne, Director of the Fermentation Laboratory of the Pasteur Institute in Lille, France, first isolated and characterized the simplest and most commonly occurring polyester of PHA, poly-3-hydroxybutyrate, PHB or poly(3HB) represented in Figure 8.16, in the 1920s [13].

The production of PHA is triggered by a microorganism such as *Alcaligenes eutrophus* under certain conditions such as lack of oxygen and excess of carbon supply. The polyester is then extracted and purified from the bacteria during the fermentation of carbohydrates such as sugar and glucose, or vegetable oil or glycerine from biodiesel production.

Poly(lactic acid) or PLA is a plastic made from corn, an annually renewable resource, leading to 100% biodegradability and compostability. Plastic products made from corn are in all common household products all around the world. The NatureWorks® PLA is derived from naturally occurring plant starch. According to the NatureWorks LLC website, the different steps of the transformation of plant sugar into NatureWorks PLA are the following [14]:

1. *Photosynthesis* (use of sunlight) used in conjunction with carbon dioxide and water create glucose (sugar) and oxygen. The plant uses the sugar as a fuel and the unused sugar gets stored as starch in the kernel of the corn.
2. After the *harvest of field corn*, it is cooked and then ground and screened to isolate the starch.
3. The starch is converted into sugar and microorganisms convert the starch into lactic acid through fermentation.
4. The lactic acid molecules form the monomer lactic acid, which then is polymerized to form the polylactide polymer. During the polymerization, tens of thousands of monomers of lactic acid are linked together.
5. The polymer PLA is then shaped into pellets, which are sold under the brand-name NatureWorks PLA, which is often found in packaging and fiber products.

The PLA polymer can be converted into a number of common products beyond simple plastic sheet. One of the most commonly seen products is compostable plastic tableware (cutlery, plates, etc.), which can result in 50% less nonrenewable

energy consumption and 60% fewer greenhouse gas emissions. Other applications include apparel, fresh food packaging, and durable goods such as computers and cell phones.

In 2000, 3 million tons of polystyrene, commonly known as Styrofoam, was made for use in disposable coffee cups and food packaging, and 2.3 million tons was thrown away. Polystyrene waste does not break down quickly and is difficult to recycle. A new strategy based on the recycling of Styrofoam into PHA was developed by a team of microbiologists at University College Dublin [15]. These scientists found that a soil bacterium, based on *Pseudomonas putida*, thrives on dirty styrene oil (C_8H_8) derived from the pyrolysis of polystyrene. In this type of reaction, the styrene is the source of carbon, which is then stored as PHA (Figure 8.17).

Highlight 8.2 focuses on a type of biodegradable plastic bottles named ENSO.

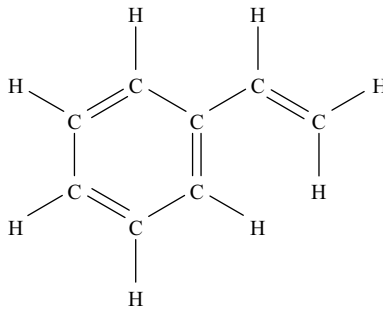


Figure 8.17. Molecular structure of styrene.

Highlight 8.2 Biodegradable Plastic Bottles: ENSO Bottles

A company named ENSO Bottles LLC and launched in 2008 is making biodegradable plastic bottles. ENSO bottles are not made of PLA or corn-based plastic. They are made of everyday plastic and an undisclosed organic additive. They have similar durability and shelf life properties as regular plastic bottles.

When these ENSO bottles are not recycled and end up in an anaerobic landfill environment, the microbes are attracted to the organic additive and eat through the plastic for food and energy. These microbes break down the ENSO bottles into biogases and inert humus. The plastic bottle making process is the same as with any other plastic with the exception of the addition of the organic compound. Thus, there is no need to change the existing process and therefore ENSO bottles are part of the natural cycle of life.

8.3.2 The Case of Compostable Chemicals

In 2010, SunChips® bags became the first fully compostable chip bag made of PLA film [16]. Researchers have found that under aerobic compost conditions (in the presence of oxygen) at $>55^{\circ}\text{C}$ the film structure completely breaks down in 12 to 16 weeks. These conditions are very similar to those used in a typical industrial compost facility. However, under anaerobic conditions commonly found in a landfill, the film would not decompose. In a home composting process under adiabatic conditions (in the absence of heat transfer) and in the presence of an ideal mixture of greens, leaves, and grass clippings, the SunChips bags completely decomposed in about 12 to 16 weeks. If the conditions are less than ideal (poor mixture of greens and browns with lower reaction temperatures) the decomposition would still take place but at a slower pace.

Highlight 8.3 focuses on composting and compostable available materials.

8.3.3 Production of Ethanol from Biomass

The production of ethanol from cellulosic biomass for automobile fuel is not a new idea. The ancient Greek society was already using agricultural products such as grains to produce ethanol. Ethanol is currently used as an alternative to gasoline in flex-fuel light vehicles in Brazil and as an oxygenate for gasoline in the United States. Most cars in the United States can function with a mixture of 10% ethanol mixed with gasoline. The main focus for the production of bio-ethanol is to use fermentation of starch or sugar present in a wide variety of crops such as sugarcane,

Highlight 8.3 Old Plastics, Fresh Dirt

It is commonly believed that waste simply biodegrades or decomposes in a landfill. However, since most landfills are kept dry and deprived of oxygen, this is not true. Waste is not supposed to biodegrade in a landfill and some biodegradable products may only be partially biodegradable. When the latter happens, groundwater pollution and gas emissions can lead to more serious problems.

Since biodegradability may not always be a favorable option, scientists have studied how to control biodegradation outside of a landfill through composting. Many compostable materials, such as bags, films, resins, food ware, and packaging items, can naturally be converted to useful products for farming or gardening.

While we all know that food, leaves, grass clippings, and garden wastes can all go into the compost pile, it is less common to throw a cup or a lid on that compost pile. This is definitely possible through the purchase of GreenGood PLA goods such as cups and cutlery that are 100% biodegradable and compostable.

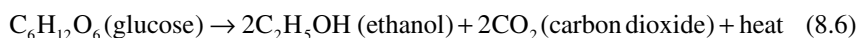
sugar beet, potato, sunflower, wheat, straw, cotton, switchgrass, manioc, corn, and any other types of cellulose-containing biomass or waste. However, growing crops for fuel raises several other sustainability questions:

1. The production of crops requires substantial consumption of fertilizer, most of which is produced from nonrenewable sources such as gas. The life cycle analysis indicates that ethanol production from crops is only marginally beneficial for the reduction of consumption of nonrenewables.
2. Social justice aspects of sustainability require that one considers the food versus fuel aspects of producing ethanol from food crops. When arable land is used for the production of fuel, less food is produced, leading to an increase in food prices and an increase in worldwide hunger.

While there are clear concerns with using food crops as a source of ethanol, other crops, such as wood-type material and specifically fibrous cellulose as a source of biomass, are likely to play a bigger role in the future. Cellulose, one of the carbohydrate polymers present in woody biomass, can serve as a potential raw material for the production of fuel ethanol.

Before ethanol can be produced from woody biomass, the cellulose needs to be released from the biomass superstructure. This can be accomplished chemically through acid pretreatment or steam explosion. Afterwards, the liberated cellulose chains are broken down through hydrolysis to produce starch and sugars. The conversion of cellulose into sugar may also be achieved through the use of enzymes and yeasts. Cellulase is usually used to hydrolyze the cellulose into glucose before the fermentation step.

Glucose is decomposed into ethanol and carbon dioxide through fermentation, per the following general reaction pathway:



Many bacteria may be used to catalyze the fermentation reaction, and depending on the choice of microorganism and the process conditions, products other than ethanol may be obtained. Microorganisms such as *Saccharomyces cerevisiae*, *Zymomonas* sp., and *Candida* sp. are well-known fermentation agents. However, *Saccharomyces cerevisiae*, commonly known as baker's yeast, can be used either in its natural form or as a genetically modified form.

There is also interest in converting biomass to butanol, since butanol is more similar to gasoline and less soluble in water. *Clostridium acetobutylicum* is the typical microorganism for the process, which is similar to the process used for production of ethanol.

It is essential to keep in mind that the selection of the appropriate enzyme and process conditions is specific to the source of biomass and the desired end product. High performance yeast strains are now selected and commercialized for dry grind corn ethanol production using batch fermentation [17]. The commercial yeast formats and fermentation conditions should be optimized. Stress factors affecting yeast

metabolism include high temperatures, high osmotic pressure, high sodium and other ions concentrations, and high concentrations of organic acids. Prevention of bacterial growth is also essential to successful ethanol production.

Fermentation may be accomplished in either a batch or continuous mode. Regardless, the rate of the reaction determines the ethanol yield and is described through traditional Michaelis–Menton kinetics. In this case, the rate of reaction is written as

$$-r_A = \frac{k[E][A]}{K + [A]} \quad (8.7)$$

where $[E]$ is the concentration of an enzyme that catalyzes the reaction, $[A]$ is the concentration of the reactant, and k and K are two different characteristic constants. This is more conventionally written as

$$-r_A = \frac{V_{\max} [A]}{K_m + [A]} \quad (8.8)$$

where V_{\max} is the maximum rate of reaction for a specific enzyme concentration. Operating under differential conditions, we substitute the rate expression into the material balance

$$[A] \frac{X}{\tau} = \frac{V_{\max} [A]}{K_m + [A]} \quad (8.9)$$

This equation is also sometimes written as Monod's equation, except the reaction velocity is replaced with the specific growth rate (μ_{\max}) for the microorganism

$$\mu = \frac{\mu_{\max} [S]}{K_m + [S]} \quad (8.10)$$

When performed in batch mode, the cell density varies with time, which impacts the overall formation of ethanol product. A typical growth curve is described in Figure 8.18.

8.3.4 The Case of Flex-Fuel Vehicles

While most automotive fuel sold in the United States contains 10% ethanol, it is also possible to power the vehicle on a blend that is primarily ethanol. The optimum blend sold in both the U.S. and European markets for flexible-fuel vehicles is E85 (mixture of gasoline containing 85% of ethanol). In Brazil, flex-fuel vehicles can operate with ethanol mixtures up to E100. The Brazilian 2008 Honda Civic flex-fuel car is built with a secondary reservoir gasoline tank. In March 2009 the first Polo E-Flex was launched in Brazil without the auxiliary gasoline tank. Ethanol-based engines can be used to power automobiles, tractors, city buses, distribution trucks, and waste collectors.

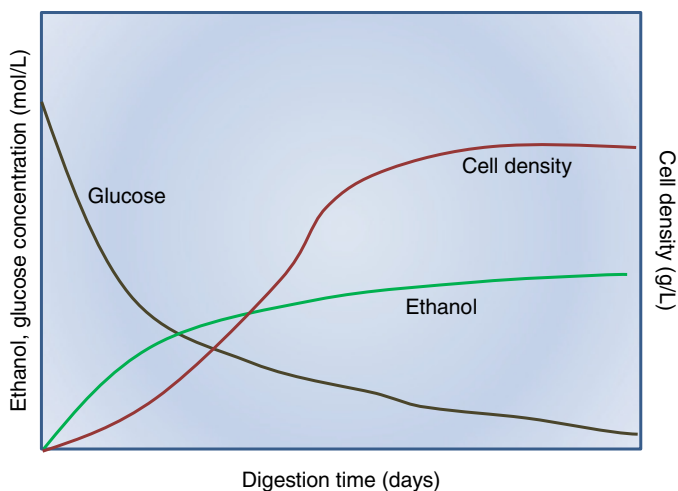
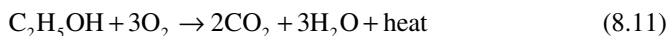


Figure 8.18. Representation of the production of cell density, and the change of glucose and ethanol concentration through digestion under anaerobic conditions.

As with any other combustion reaction, ethanol reacts with oxygen to form carbon dioxide and water, releasing significant amounts of heat:



The high temperature that is generated from combustion and the large volume of combustion gases cause substantial pressure accumulation in the engine cylinder chamber, which pushes back on the piston through the transfer of work.

In order to start the combustion reaction, there must be sufficient concentrations of air and fuel in the vapor phase, and a spark to ignite the mixture. During cold weather, the vapor pressure of ethanol is insufficient to generate enough ethanol in the vapor to spark the ignition. This problem can be alleviated by including a small secondary gasoline reservoir, which allows the car to start on pure gasoline at low temperatures, as is typical of Brazilian flex-fuel vehicles.

The United States and Brazil are the world's top ethanol fuel producers accounting together for 70% of the world's production and nearly 90% of ethanol used for fuel. The production of ethanol in Brazil is more than 30 years old and is stimulated through low-interest loans for the building of ethanol distilleries as well as tax incentives provided to the buyers of ethanol vehicles. There are no pure gasoline run vehicles in Brazil. It is now mandatory for light vehicles to run on a blend of ethanol (20%) with gasoline. The development of flex-fuel technology is now spreading across the motorcycle industry.

8.3.5 Production of Biodiesel

Biodiesel is a nontoxic and biodegradable diesel fuel equivalent made from plant oils, chemically converted to alkyl esters. The most common feedstock is vegetable oil such as soybean or corn oil (either virgin or used), but other sources including animal fats such as tallow, lard, or chicken fat may also be used. It is also possible to produce bio-oil from algae used to treat sewage waste. Production of biodiesel requires the conversion of the long-chain fatty acids in the oil into a triglyceride through chemical reaction. Depending on the source of the oil, different process conditions are required and different yields can be obtained.

Biodiesel can be used in its pure form (B100) or blended with petroleum diesel (a common blend is known as B20, a mixture of 80% petroleum diesel and 20% biodiesel). Biodiesel is not raw vegetable oil, but rather is a product derived from the oil. Biodiesel has a slightly lower fuel value than petroleum diesel, but has greater lubricity than current low sulfur diesel fuel. Biodiesel also has a higher flash point, and will gel at low temperatures of about -10°C , making use in cold weather conditions difficult. Biodiesel is compatible with most parts in commercial diesel engine systems, and thus could almost be used as a drop-in replacement in trucks, buses, boats, and construction equipment. However, the difficulties associated with low-temperature operation and the potential degradation of plastic parts in the fuel system have made the B20 blend the typical fuel associated with biodiesel use.

The process of esterification used for the production of biodiesel involves a chemical reaction of a fat or a vegetable oil with an alcohol, usually methanol, in the presence of a catalyst like sodium or potassium hydroxide (KOH). This is the preferred process, because it operates at low temperature and pressure and achieves high conversion (98%). The products are glycerine and fatty-acid methyl esters or biodiesel consisting of straight saturated and unsaturated hydrocarbon chains. The methanol is usually in excess to provide quick conversion but is recovered for reuse. In this first route nothing is wasted [18]. The inputs are alcohol (12%), catalyst (1%), and oil (87%). The outputs are alcohol (4%), fertilizer (1%), glycerine (9%), and methyl ester (86%). It is also possible to produce biodiesel through acid-catalyzed esterification of the oil with methanol, or by conversion of the oil to fatty acids and then to alkyl esters using acid catalysis.

Instead of purified vegetable oil, recycled grease can also be used as a starting material for biodiesel production. In this case, an acidic esterification comprising sulfuric acid and methanol is the first step before the transesterification can occur. The basic technology is summarized in Figure 8.19.

Biodiesel can also be produced from algae grown on waste biomass. The requirements for algae growth are just a few: carbon dioxide, sun, and water. Algae can grow under any conditions: high or low temperatures, acidic or alkaline environments, and any level of salinity. Algae-growing facilities can be built anywhere and the agricultural land is not depleted to the extent of crops grown for fuel production. The production of biofuels from biomass, such as agricultural waste, is appealing from multiple points of view:

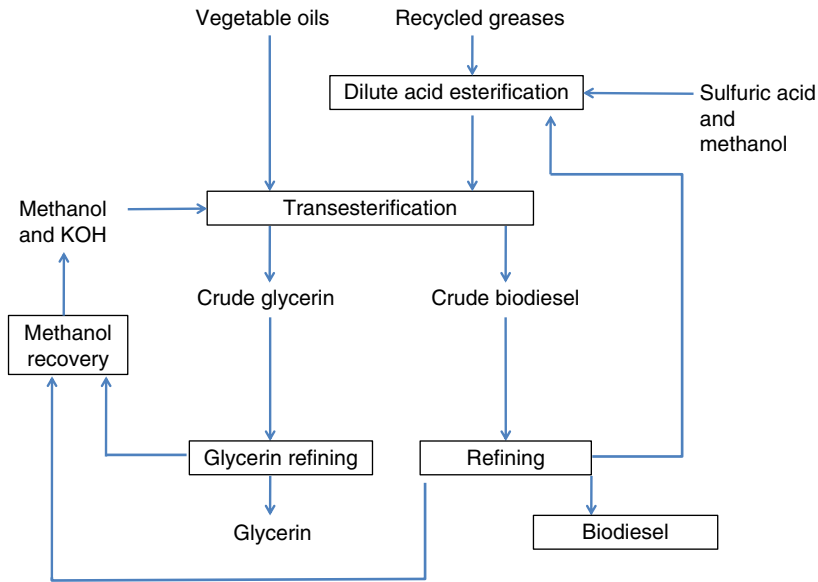


Figure 8.19. Basic technology for the production of biodiesel.

1. The feedstock is not dependent on the availability of fossil fuels.
2. Burning biofuels decreases the net amount of carbon dioxide rejected into the atmosphere since the amount of carbon dioxide given off in the process should be similar to the amount originally absorbed by the biomass.
3. The use of genetically engineered organisms can produce biofuels more efficiently and lead to a cost-competitive energy production.
4. Waste biomass can be used as the food on which algae are grown, and this growth process does not compete with the need to produce food for animal or human consumption.

The key to successful growth of algae is the correct identification of strains with the highest oil content as well as the development of cost-effective growing and harvesting methods. Algae can be grown either in ponds or lakes or in closed, translucent tubes or containers called photobioreactors. One of the challenges with converting algae to fuel is harvesting the algae from the growth medium, which tends to be easier in closed systems. The use of microalgae with high growth rates, high lipid production, and relative ease of handling in conventional reactor systems has increased the availability of biodiesel and other bio-based fuel resources.

Biodiesel 2020, a study exploring the opportunities for biodiesel fuel through the next decade, projects a rapid growth in the production of biodiesel from algae [19]. Some growth areas include:

1. Capture the carbon dioxide from the smokestacks of a power plant and use the carbon to produce algae for low-emissions biofuels for transport.

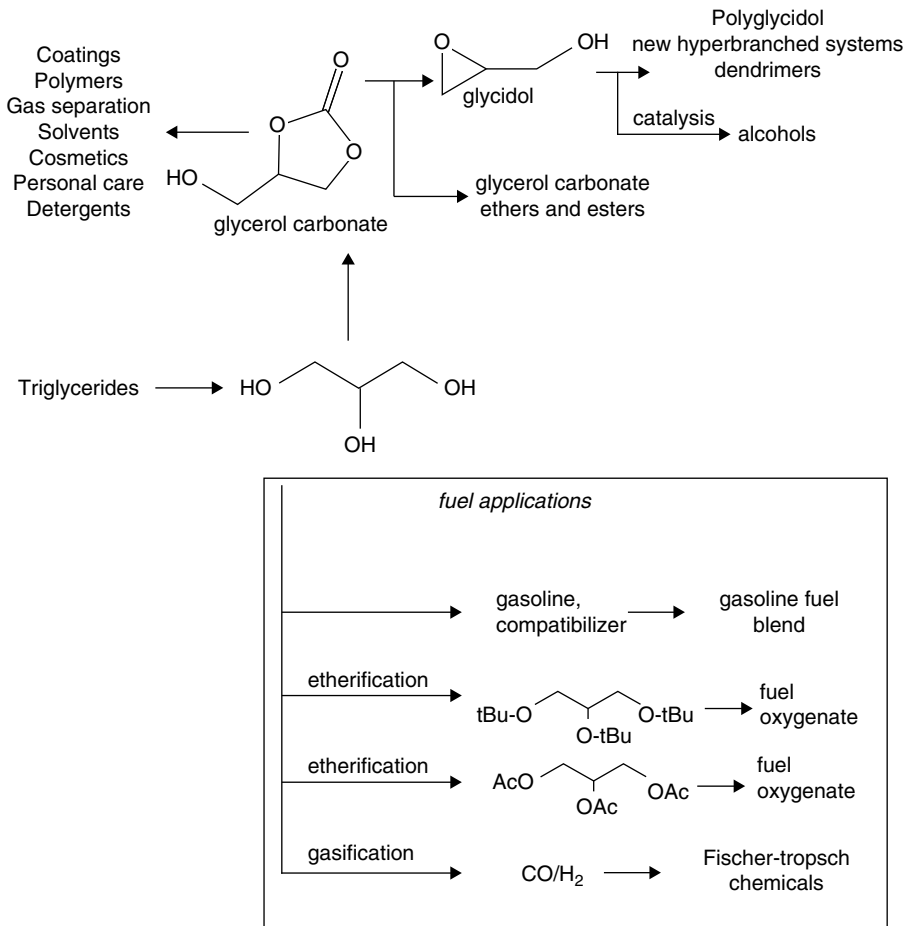


Figure 8.20. Triglycerides as the building blocks for a biorefinery.

2. Use the entire algae plant mass and convert it via a biomass-to-liquid (BTL) thermochemical process to create bio-oil or bio-crude oil, which can then be reprocessed into diesel.
3. Use waste water from municipalities to grow algae.

Some of these opportunities are already present today. The company GreenFuels uses algae to capture and convert the carbon from coal-power generation sources into biodiesel or ethanol for transport fuel. Other private ventures, such as PetroAlgae, are finding ways to expand the production of algae oil using large open pond technology. A public-private venture between UOP (a division of Honeywell) and the U.S. Defense Advanced Research Project Agency is working toward the conversion of algae into military grade jet fuel.

While the oils associated with vegetable matter and those pressed from algae used in waste treatment processes are most typically converted to biodiesel fuel, it is also possible to produce a broad range of products from vegetable oil and animal fats. These products can then once again serve as the basis for the production of chemicals from renewable resources (Figure 8.20). As with all bio-based products, it is important to complete a full economic and environmental life cycle analysis to determine the most viable routes for desired products.

8.4 CONCLUSION

The use of renewable materials for chemicals and energy production is becoming increasingly attractive as realization grows that fossil resources are limited. While there are other choices for the production of energy, which will be covered in Chapter 9, the conversion of biomass represents a real alternative for production of chemicals. Thus, the growth and expansion of the integrated biorefinery is of significant interest for the modern chemical company.

The Office of Biomass Energy in the Department of Energy has a significant research program focused on better technologies for using biomass resources, and while it is primarily focused on energy production, it also addresses the conversion of renewables for chemicals. Its program encompasses activities well beyond the traditional scope of the chemist and the chemical engineer, from achieving greater yield during crop growth, to the use of new fertilizers and pesticides, conversion of biomass into energy and chemicals, and ultimately waste disposal.

Several issues remain to be resolved. For one, it is not typically cost effective for large-scale production from renewable resources. Sourcing is a concern, and it is unclear whether there are sufficient biomass resources available to meet societal demands. The intermittency of biomass availability is also an issue. All of these aspects need to be considered in the evaluation of what may ultimately become the major source of chemicals and energy for the future.

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