Processing of Oleaginous Biomass

9.1 Introduction

Oleaginous biomass includes traditional oil seed crops such as rapeseed and soybeans, unconventional crops such as jatropha and jojoba, aquatic species such as microalgae, and even animal manure and sewage. In some cases lipid content is high enough to justify its recovery through mechanical pressing or solvent extraction. When lipid is difficult to separate from biomass due to low concentration or challenging substrate or the lipid-rich remnant is to be utilized, other approaches are employed to recover energy from these feedstocks. These alternatives include hydrothermal processing and pyrolysis, which produce energy-rich organic liquids suitable for upgrading to liquid fuels, and anaerobic digestion to produce methane.

9.2 Lipids

Lipids were historically defined as compounds of biological origin that are soluble in organic solvents. Lipids include terpenes and esters of fatty acids. Terpenes include a large number of hydrocarbons that occur naturally in many plants, some of which have been significant sources of biobased products for thousands of years. Esters of fatty acids produced in plants and a variety of microorganisms include waxes and triglycerides. The energy-rich triglycerides, esters of glycerol and long-chain fatty acids, are of particular interest in the production of biobased products.

9.2.1 Triglycerides

Triglycerides, also known as fats and oils, are esters of glycerol and fatty acids. Recall that fatty acids are long-chain carboxylic acids containing even numbers of carbon atoms. The acid fractions of triglycerides can vary in chain length and degree of saturation. Fats, which are solid or semi-solid at room temperature, have a high percentage of saturated acids, whereas oils, which are liquid at room temperature,

have a high percentage of unsaturated acids. Plant-derived triglycerides are typically oils containing unsaturated fatty acids, including oleic, linoleic, and linolenic acids.

9.2.2 Terpenes

Terpenes are any of various isomeric hydrocarbons $(C_5H_8)_n$, where n is 2 or more, originally derived from turpentine, an oleoresin obtained from coniferous trees. Terpenes, abundant in a variety of plants, are responsible for the odors of pine trees and the color of carrots and tomatoes.

Structurally, terpenes consist of two or more isoprene units joined together, which is called a conjugated diene, a compound containing two double bonds of carbon joined by one single bond. These compounds may have different degrees of unsaturation and a variety of functional groups. Terpenes range from relatively simple hydrocarbons to large polymeric molecules (polyisoprenes). Terpenes from conifers were the source of naval stores, the resinous substances used to maintain wooden ships and ropes. Polyisoprenes from the hevea rubber tree (*Hevea braziliensis*) or the guayule shrub (*Parthenium argentatum*) are the basis for natural rubber.

The hydrocarbon content of plants is a small fraction of the total plant material. Typical terpene content of mesophytic biomass species is only 0.5–1.5 wt%. Thus, economic recovery historically required tapping of living biomass, as is done with hevea rubber trees, or recovery as a coproduct in the processing of other biomass components, such as the production of turpentine as part of wood pulping. More recently, genetic engineering has been used to isolate genes for terpene biosynthesis and optimized its expression in yeast or bacteria, which can then be cultured in bioreactors with the goal of producing commercially significant quantities of hydrocarbons for fuels and other applications.

9.3 Lipid Extraction

Extraction of lipids from oil seeds is relatively straightforward. The seeds are crushed to release the oil from the seed. Mechanical pressing is used to extract oil from seeds with oil content exceeding about 20%. Solvent extraction is required for seeds of lower oil content. The residual seed material, known as meal, is used in animal feed.

Extraction of lipid from microalgae is still under development. Lipids can be extracted from either dry algal biomass (10–15% moisture) or wet algal filter cake (80% moisture). Lipid extraction from dry algal biomass can be accomplished in a manner similar to lipid extraction from oil seeds, using either mechanical pressing or solvent extraction. Products include lipid and dry algal remnant. However, significant thermal energy is consumed in drying the algal biomass even when starting

with filter cake. Lipid extraction from wet filter cake is not well developed but is envisioned to include disrupting the cell wall (lysis) either through mechanical treatments such as ball milling and mixing with a solvent such as hexane to dissolve the lipids. The mixture is decanted to recover the solvent phase containing the lipids, an aqueous phase, and wet algal remnant. A multiple effect evaporator is used to separate the lipid from the hexane, which is recycled.

Triglycerides, in principal, can be directly used as fuel in diesel engines. However, their high viscosity results in frequent fouling of the injectors and rings in diesel engines. Triglycerides can be chemically modified to reduce their viscosity and improve their fuel properties. Most widely practiced today is transesterification of triglycerides to biodiesel although hydrotreating is likely to find wider application if plentiful sources of inexpensive lipids can be developed.

9.4 Transesterification of Triglycerides

Transesterification describes the process by which triglycerides are reacted with methanol or ethanol to produce methyl esters and ethyl esters, respectively, along with the coproduct glycerol. For example, one triglyceride molecule reacts with three methanol molecules to produce one molecule of 1,2,3-propanetriol (glycerol) and three ester molecules:

$$(9.1)$$
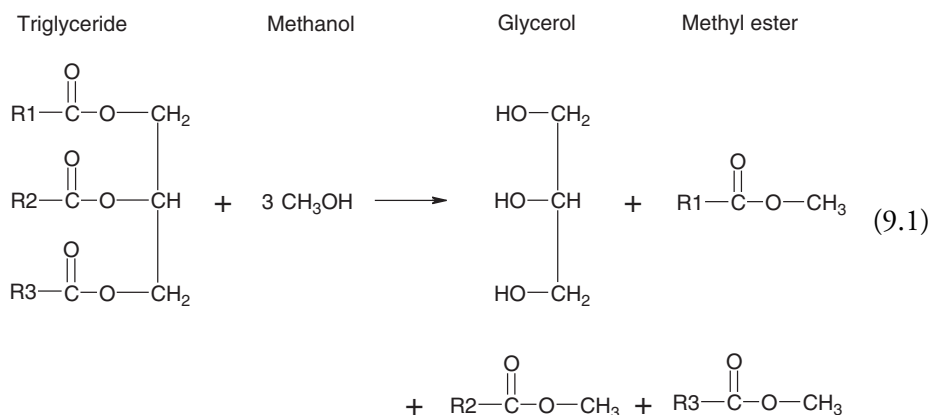
Near quantitative yields of methyl (or ethyl) esters can be produced in 1 hour at room temperature using 6:1 molar ratios of alcohol and oil when catalyzed by 1% lye (NaOH or KOH).

The lye also serves as a reactant in the conversion of esters into salts of fatty acids. These salts are familiarly known as soaps and the process is called saponification (soap forming). Small amounts of soap are also produced by the reaction of lye
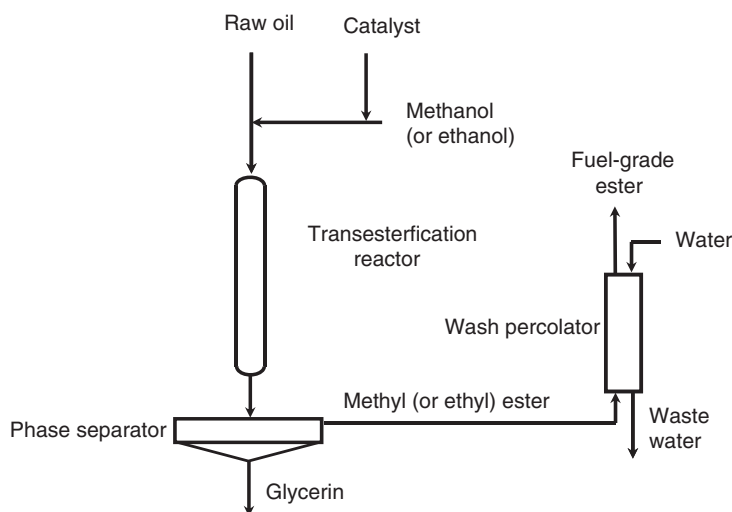
FIG. 9.1   Conversion of triglycerides to methyl (or ethyl) esters and glycerol.

with fatty acids. Upon completion, the glycerol and soap are removed in a phase separator. A flow sheet for a biodiesel production facility is given in Figure 9.1.

The name biodiesel comes from the fact that plant-derived methyl esters have combustion properties similar to the fuels designed for diesel engines. Nevertheless, biodiesel is chemically distinct from petroleum-derived diesel with the result it is not a perfect diesel fuel substitute. Like the lipids from which they are obtained, fatty acid methyl esters are subjected to microbial or oxidative attack, making them unsuitable in applications requiring long-term fuel storage. Low-temperature operability has occasionally been a problem. Whereas petroleum-derived diesel can be formulated from a broad range of hydrocarbons to give desired properties, the range of plant-derived triglycerides is more constrained for the production of biodiesel. Long-chain methyl esters and biodiesel contaminants such as sterol glycosides can solidify at low temperatures, causing fuel filters to plug. Other disadvantages of biodiesel are the consumption of fossil fuel–derived methanol in its manufacture and the generation of low-value glycerin as a major coproduct.

9.5 Catalytic Upgrading of Triglycerides

An alternative to transesterification of triglycerides to produce methyl ester and glycerin is catalytic upgrading to synthetic gasoline or diesel. If triglycerides are first pretreated to remove alkali metals and other contaminants, they can be mixed

with vacuum gas oil, one of the heavier cuts from vacuum distillation of petroleum, and cracked to gasoline range molecules in a fluidized catalytic cracker (FCC) in a petroleum refinery.

Alternatively, triglycerides can be hydrotreated to produce synthetic diesel in two steps. The first step removes alkali metal and other contaminants and saturates carbon–carbon double bonds in the fatty acid chains, which are responsible for the tendency of lipids to go rancid over time. By hydrogenating these to single bonds, the stability of the fuel is improved. The second hydrotreating step separates the fatty acids from the glycerin backbone of the triglycerides. It also removes the oxygen atoms responsible for the acidic nature of fatty acids, either by hydrodeoxygenation or decarboxylation (removal of oxygen as carbon dioxide), transforming these long-chain molecules into hydrocarbons. Furthermore, hydrogen reacts with the glycerol to form propane, a commercially important gaseous fuel.

The nature of the long-chain hydrocarbons formed from hydrotreating triglycerides depends upon the lipid feedstock. Rapeseed, for example, produces mostly hydrocarbon chains containing 16, 18, or 22 carbon molecules. Thus, these hydrocarbons can rightly be described as diesel fuel since petroleum-based diesel contains hydrocarbons containing between 10 and 22 carbon atoms (although there are some differences in the arrangement of these carbon atoms).
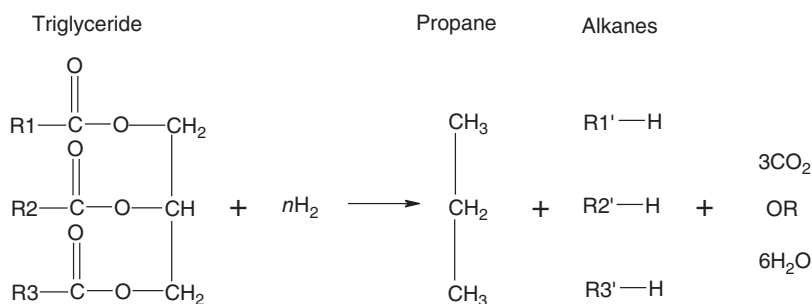
Hydrotreating vegetable oils and animal fat to produce synthetic diesel fuel has been demonstrated at large scale. The propane and other light hydrocarbons produced are used to generate hydrogen needed for hydrotreating. Wide scale commercial deployment awaits greater supplies of low-cost lipid feedstocks.

The use of refinery hydrotreaters presents important advantages over other approaches to advanced biofuels since it reduces the capital cost of biorefinery infrastructure and allows accelerated deployment of the technology if sufficient quantities of lipid feedstock can be procured. It also raises concerns among those who imagined lipid-based biofuels would always be the province of farmer-entrepreneurs. However, even the first generation of lipid-based manufacturing

plants have shifted over time from a few million gallons per year to several tens of millions of gallons capacity including a couple of plants in the United States of about 100 million gallons capacity. Economies of scale are as important to biorefineries as they are for petroleum refineries although the optimal sizes are likely to be quite different because of constraints in moving solid, low-density biomass to processing facilities.

9.6 Other Processing Options for Oleaginous Biomass

Although oleaginous biomass is rich in lipids, as shown in Figure 9.2, it also contains large amounts of other components including carbohydrate and protein. Soybeans contain 20 wt% lipids, but they also contain almost as much carbohydrate and twice as much protein. Even particularly lipid-rich strains of microalgae have more mass associated with the non-lipid components of their biomass. Simply extracting lipid from algal biomass and landfilling or land applying the remnant would be very wasteful of this biorenewable resource.

As shown in Figure 9.3, dry algal remnant could be pyrolyzed to bio-oil suitable for upgrading to transportation fuels. It could also be catalytic pyrolyzed to aromatic hydrocarbons. The wet algal remnant requires processes that are tolerant of high moisture feedstocks. Wet processing options include hydrothermal processing and anaerobic digestion. Although algal remnant mostly contains carbohydrate and protein, pyrolysis, hydrothermal processing, and anaerobic digestion are also able to convert lipid into value-added products. Thus, an alternative to extracting lipid and processing it separately from the algal remnant is to directly process the whole algal biomass. The following sections explore these possibilities.
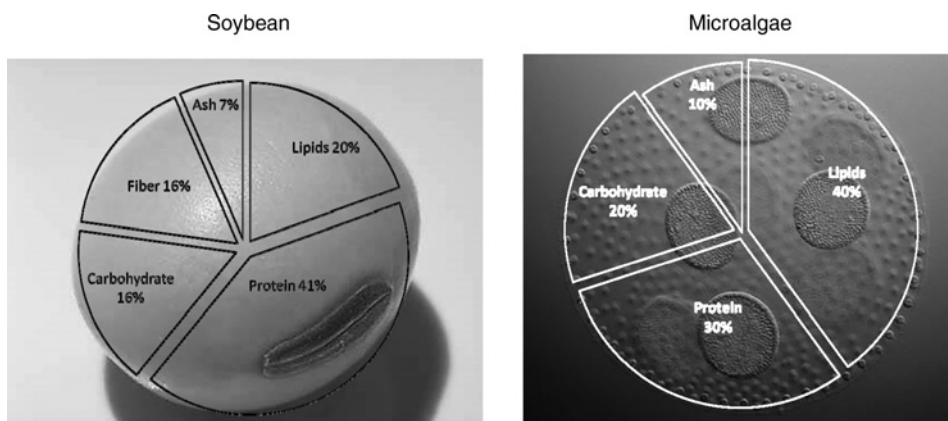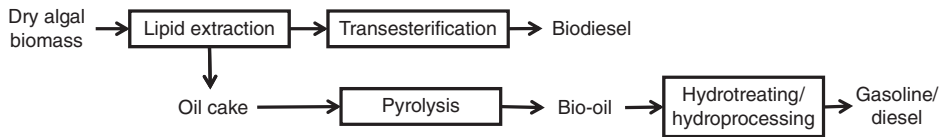
Soybean   Microalgae

FIG. 9.2   Most kinds of oleaginous biomass are both lipid and protein rich.

(a)

Dry algal biomass → Lipid extraction → Transesterification → Biodiesel

Oil cake → Pyrolysis → Bio-oil → Hydrotreating/ hydroprocessing → Gasoline/ diesel

(b)

Wet algal filter cake → Lipid extraction → Hydrotreating → Diesel / Propane

Algal remnant

Hydrothermal processing → Hydrotreating/ hydroprocessing → Gasoline/ diesel
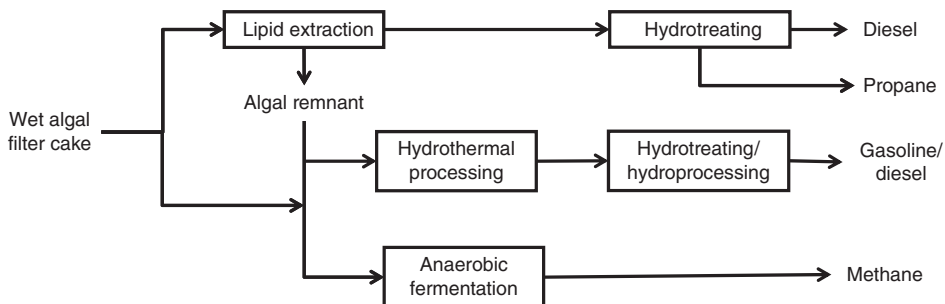
Anaerobic fermentation → Methane

FIG. 9.3   Possible processing routes for algal biomass: (a) dry processing; (b) wet processing.

9.6.1 Pyrolysis of Lipid-Rich Biomass

Pyrolysis is able to convert either whole algal biomass or algal remnant into a liquid product similar to the bio-oil produced from lignocellulosic biomass, as described in Chapter 8, but there are important differences. Because neither algal biomass nor algal remnant contains lignin, the oil does not contain the phenolic oligomers found in the bio-oil from lignocellulosic biomass. Lipids are converted into fatty acids or even alkanes, which are desirable from the standpoint of upgrading bio-oil. However, the protein in algal biomass and remnant are converted in part to a variety of nitrogenous compounds including pyrroles, nitriles, indoles, pyridines, and poly-heteroaromatic compounds. These molecules would have to be removed (by hydrotreating) to prevent them from poisoning upgrading catalysts or producing unacceptable nitrogen oxide emissions during combustion.

On the other hand, if algal biomass or remnants are pyrolyzed in the presence of a zeolite catalyst, the biomass is both denitrified and deoxygenated to produce aromatic hydrocarbons as the only major condensable organic compounds. Most of the nitrogen is converted to ammonia, a valuable fertilizer, or sequestered in the coke product. The aromatics, which are mostly benzene, toluene, and xylene, are high-value commodity chemicals and important blendstocks for enhancing the

octane rating of gasoline. The process is still under development but offers the prospect of directly converting algal biomass or remnant into high-value chemicals and fuels.

9.6.2 Hydrothermal Processing of Oleaginous Biomass

Hydrothermal processing, as described in Chapter 8, is a form of solvolysis with water serving as the solvent. Accordingly, it is extremely attractive for processing high moisture feedstocks like manure or microalgae, eliminating feedstock drying prior to thermochemical processing. Although the discussion of hydrothermal processing in Chapter 8 focused on lignocellulosic biomass, in many ways it has even better prospects for processing oleaginous feedstocks.

Carbohydrate in microalgae, because it is not embedded in a matrix of lignin, is more readily hydrolyzed to monosaccharides than the carbohydrate in lignocellulosic biomass. Lipids readily hydrolyze to fatty acids and glycerol at 250°C and 5 MPa. The free fatty acids, in turn, can be decarboxylated to form long-chain hydrocarbons especially in the presence of a base catalyst. Protein hydrolyzes to amino acids at relatively mild hydrothermal conditions (around 250°C) although yields are rarely more than 10–15 wt% since the amino acids subsequently decompose. However, hydrothermal processing of biomass is frequently conducted at more severe conditions with the goal of producing a mixture of organic compounds. As Figure 9.4 illustrates, liquefaction of oleaginous biomass produces a water insoluble biocrude, an aqueous phase, a residue that includes char, and gas. The biocrude resembles bio-oil except that it contains less water, is less oxygenated, and
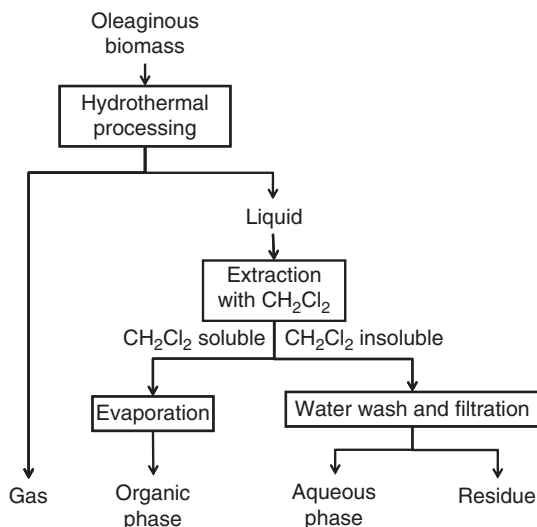

Fɪɢ. 9.4 Liquefaction of oleaginous biomass through hydrothermal processing.

is more viscous. Like bio-oil, it can be hydrotreated and hydrocracked to gasoline and diesel.

9.6.3 Anaerobic Digestion of Oleaginous Biomass

Biomass grown in aqueous environments presents special challenges to lipid recovery. Microalgae especially thrive under low population densities. High yields of oil are made possible by continuously harvesting low-density suspensions of microalgae from their aqueous environment. Dewatering these low-density suspensions requires a 500-fold concentration of the microbial biomass, which represents one of the major challenges in the production of algae-based fuels.

An alternative to directly harvesting the algae is to anaerobically digest them into a more easily recoverable fuel. Anaerobic digestion is the decomposition of organic matter, including polysaccharides, proteins, and lipids, into simpler compounds by bacteria in an oxygen-free, aqueous environment. It is widely used to treat municipal solid waste (MSW), municipal and industrial wastewater, and increasingly animal manure for the purposes of pollution control. The process occurs in stages, each involving specific types of bacteria, to successively break down the organic matter into simpler organic compounds. Complete digestion produces biogas, a gaseous mixture of CH_4, CO_2, and some trace gases, and a solid residue known as sludge.

Anaerobic digestion arises naturally in marshy ground and landfills. The English gave the name "will-o'-the-wisp" to the mysterious, ephemeral flames that appeared spontaneously in marshlands as a result of decaying vegetation. The origin of this flammable gas was recognized by the middle of the seventeenth century but not exploited until the end of the following century when gas from sewage was used for street lighting in England and power in India. These early systems were difficult to operate and maintain, and hydrogen sulfide in the gas corroded pipes and engines. Today, the technology is well developed for production of methane-rich gas from almost any kind of feedstock with the possible exception of lignins and keratins.

Fundamentals of Anaerobic Digestion

The complete anaerobic degradation of organic matter is a three-stage process. As illustrated in Figure 9.5, diverse bacterial consortia are involved in the hydrolysis, fermentation, acidification, and methanogenesis of the various components of biomass. The first step involves hydrolysis of polysaccharides to oligosaccharides and monosaccharides, of proteins to peptides and amino acids, of triglycerides to fatty acids and glycerol, and of nucleic acids to heterocyclic nitrogen compounds, ribose, and inorganic phosphate. Hydrogen and carbon dioxide are also produced. Coliform bacteria, such as the pathogen *Escherichia coli* and pathogens in the genera *Salmonella* and *Shigella*, are common fermentative bacteria.
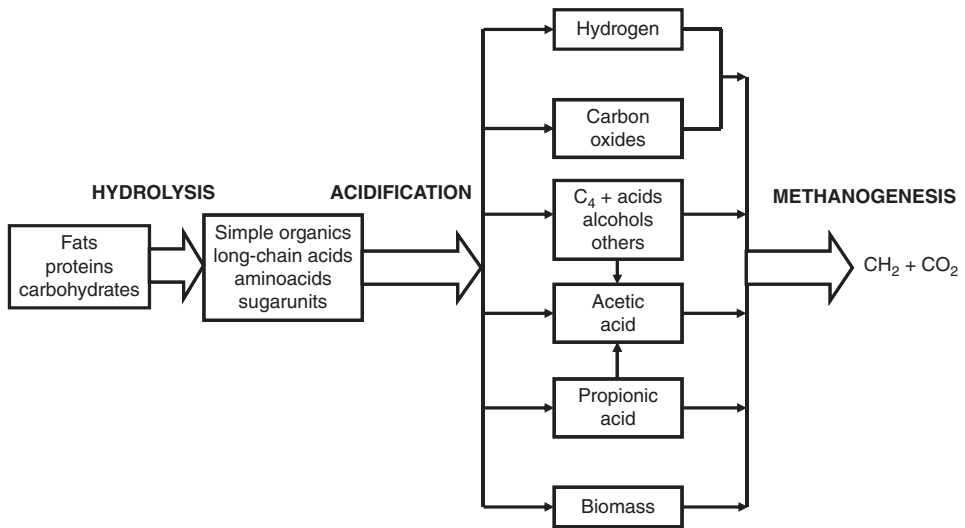
FIG. 9.5 Microbial phases in anaerobic digestion. Adapted from Klass, D.L. (1998) *Biomass for Renewable Energy, Fuels, and Chemicals*. San Diego: Academic Press.

This step is followed by transitional digestion through the action of aceto-genic (acid-forming) bacteria. Products of fermentation that are too complex for methanogenic (methane-forming) bacteria to consume are further degraded in this step to acetate, H_2, and CO_2. Traces of oxygen in the feedstock are consumed in this step, which benefits oxygen-sensitive, methanogenic bacteria. Furthermore, nutrients such as ammonium salts from degradation of proteins are released. The final step, methanogenesis, converts acetate to CH_4 and CO_2 by the action of methanogenic bacteria. Furthermore, H_2 and CO2 released during acetogenesis are converted to additional methane. About 70% of the methane and carbon dioxide is produced from acetate and 30% is produced from carbon dioxide and hydrogen. The methanogenic bacteria lower the acidity of the fermentation broth, which is beneficial to acetogenesis since the acid-producing organisms are sensitive to high acidity.

Advantages of anaerobic digestion for processing biomass include the use of non-sterile reaction vessels; automatic product separation by outgassing; and rel-atively simple equipment and operations. The primary disadvantages are slow reaction rates and low methane yields. The breakdown of cellulose to sugars may require reaction times as long as a month to achieve high yields of methane. Some plant components are resistant to microbial degradation. Lignin, in particular, is only slowly converted because of its stable polyaromatic structure. Although the theoretical weight yield of methane from glucose is 27 wt%, the complex of lignin and cellulose known as lignocellulose in plant materials results in substantially

Table 9.1 Anaerobic digestion yields of biogas for various feedstocks

Feedstock	Biogas Yield (m³/kg of Volatile Solids)
Wastewater	0.094–0.31
Human sewage	0.37–0.94
Distillery waste	>0.69

Source: Wyman, C.E. (1994) Alternative fuels from biomass and their impact on carbon dioxide accumulation. *Applied Biochemistry and Biotechnology*, 45/46, 897–915.

lower yields of methane than might otherwise be expected from cellulose. Another disadvantage is microbial reduction of sulfate and other sulfur compounds to hydrogen sulfide, a toxic, corrosive gas that complicates the use of biogas.

Anaerobic Digestion Equipment

All anaerobic digesters produce two effluent streams: biogas and sludge. Most digestion systems produce biogas that is between 55% and 75% methane by volume with the balance being carbon dioxide along with traces of hydrogen sulfide. The amount of biogas produced depends on both the composition of the feedstock and the design of the digester. Table 9.1 gives the range of gas yields expected for various feedstocks in terms of the volatile solids content of the material. Volatile solids are defined as the weight loss from a dried solids sample after firing in a muffle furnace at 550°C.

Anaerobic digesters can be broadly characterized as single-tank or two-tank reactors (also known as conventional or two-phase reactors, respectively). The single-tank reactors, illustrated in Figure 9.6, can be operated in one of the several modes: batch, intermittent, or continuous.

In the batch mode, the reactor is loaded with feedstock only once and microbial reactions are allowed to proceed to completion. Only gas is removed during the process. Batch reactors are inherently non-steady in their operation, which prevents optimum feedstock throughput and biogas yields. Thus, they are relegated only to the smallest digester systems.

The intermittent mode periodically adds additional feedstock as aqueous slurry while drawing off an equal volume of fermenter broth. Stratification occurs within the reactor, consisting of an active layer of digesting solids, an inactive layer of stabilized (indigestible) solids at the bottom, and a supernatant layer at the top. The surface of the supernatant layer is usually covered with a thin layer of scum. The challenge of this mode is retaining the sludge until it is fully digested. One way to improve efficiency is to encourage movement of feedstock through the active biosolids where the microorganisms reside. The intermittent mode requires retention times of 30–60 days and has loading rates of 0.5–1.5 kg per day of volatile solids per cubic meter capacity.
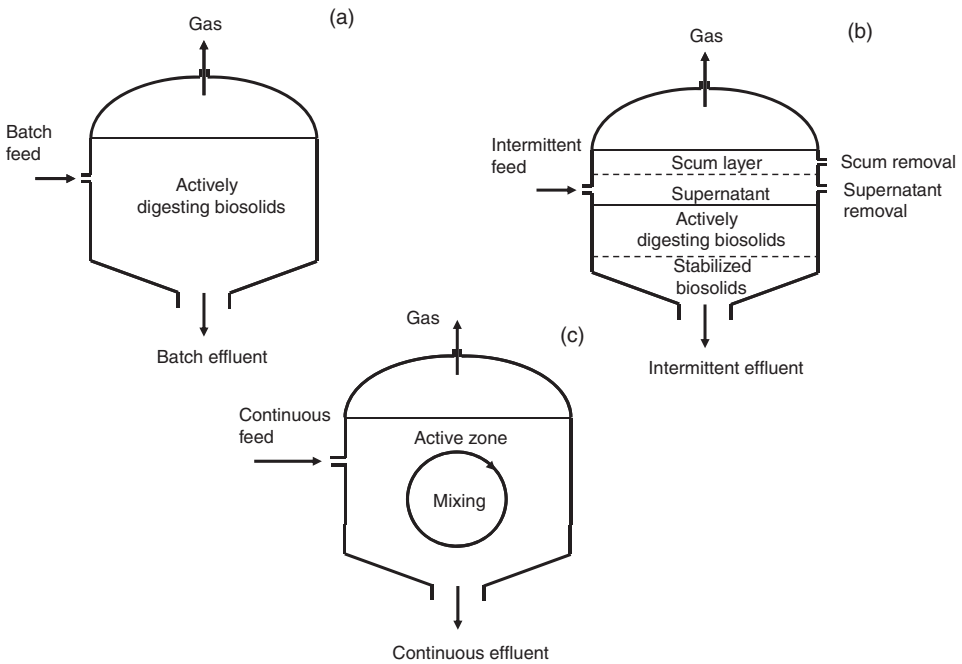
FIG. 9.6 Types of anaerobic digesters: (a) batch fed; (b) intermittently fed; (c) continuously stirred and fed.

Higher rate digestion can be achieved in continuous mode operation of single-tank reactors. Mixing is used to provide homogeneity. Retention times are 20 days or less and loading rates are 1.6–6.4 kg per day of volatile solids per cubic meter capacity.

Two-tank reactors, illustrated in Figure 9.7, were developed in response to the observation that methanogenesis appears to be the rate-limiting step in anaerobic
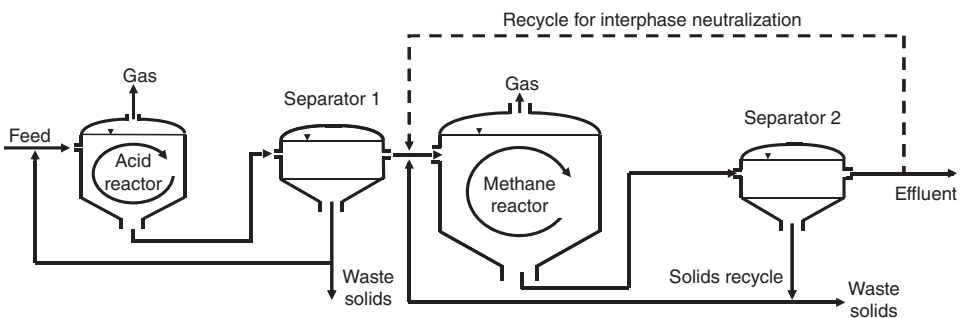

FIG. 9.7 Two-phase anaerobic digesters.

digestion. Two-tank reactors physically separate the acid formation and methane formation phases of digestion so that each takes place under optimal conditions. Benefits of this technology are numerous: hydrolysis and acidification occur more quickly than in conventional systems; the common problems of foaming in single-tank systems are reduced by the destruction of biochemical foaming agents before they reach the methane-forming reactor; and the biogas produced is typically rich in methane.

The biological conversion process of anaerobic digestion can be used for a wide range of feedstocks of medium-to-high moisture content. Sewage sludge is most commonly used as feedstock for anaerobic digesters, but MSW, food processing wastes, agricultural wastes, Napier grass, kelp, bagasse, and water hyacinth can also be digested. Digesters are designed to maintain optimal conditions for a specific type of waste. Waste pretreatment, heating, mixing, nutrient addition, specialized bacteria addition, and pH adjustment can be manipulated to control digester performance.

Biogas, once treated to remove hydrogen sulfide, can substitute for natural gas in many applications, including stationary power generation. The carbon dioxide can be recovered and sold, and the digested solids are often marketable as fertilizer, animal bedding, and sometimes as animal feed. The digested solids have higher nutrient values per unit mass than the undigested feed solids and are effectively slow-nitrogen-release fertilizers.

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