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Biomass Conversion Processes For Energy Recovery

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Transformation of waste materials into energy can generally be accomplished through biological, thermal, and chemical processes. The energy produced from these processes can be in the form of heat, gas, or liquid fuel.

This chapter is organized into three parts. Part 1 deals with anaerobic digestion process which is used to convert waste material into biogas composed of methane and carbon dioxide. Major emphasis is given to the recovery of energy from the organic fraction of MSW, as there are numerous commercial-scale digesters in operation throughout the world using processed MSW as a source of feedstock. In Part 2, the focus is on chemical conversion processing of biomass for the production of liquid fuel. Part 2 deals with combustion and gasification processes for the generation of electric power. In Part 3, the focus is on converting biomass into liquid fuels.

25.1 Energy Recovery by Anaerobic Digestion

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25.1.1 Introduction

The anaerobic digestion process, carried out in the absence of oxygen, involves the use of microorganisms for the conversion of biodegradable biomass material into energy, in the form of methane gas and a stable humus material. Anaerobic digestion can occur under control conditions in specially designed vessels (reactors), semi-control conditions such as in a landfill, or under uncontrolled conditions as it does in the environment. The focus in this part of Chapter 24 is on controlled anaerobic digestion process. It should be noted that anaerobic digestion is differentiated from anaerobic fermentation, which is the term usually applied to processes employing anaerobic microbes for the production of fermentation products such as alcohol, or lactic acid.

To describe anaerobic conversion of the biodegradable organic fraction of waste materials into energy, the following topics are examined in this chapter: (1) organic wastes and biomass used as feedstocks in anaerobic digestion process, (2) issue of organic waste biodegradability, (3) fundamental of anaerobic digestion process, (4) monitoring of anaerobic digestion process, (5) reactor types used in for anaerobic digestion, (6) modes of operation for anaerobic digestion, (7) utilization of an in-vessel anaerobic digestion process by-products, and (8) commercial-scale in-vessel anaerobic digestion technologies.

25.1.2 Organic Wastes and Biomass Used as Feedstocks in Anaerobic Digestion Process

The general scheme for a controlled anaerobic digestion process is shown in Figure 25.1. As shown, the recovery of energy involves feedstock preparation, methane gas generation, stabilization of digested solids, and the utilization of digester gas and humus as a source of energy and soil amendment, respectively. Major sources of waste materials considered as a feedstock for anaerobic digestion process are (1) municipal solid wate (MSW), (2) agricultural animal waste, (3) crop residues, biomass, and energy crops, and (4) wastewater treatment plant sludge (WWTPS). The typical composition of MSW in the U.S. is shown in Figure 25.2. The composition of MSW may vary greatly by season, geographical area, and community socio-economic level. The extrapolation of results from one location to another, therefore, may not be valid and should be done with caution.

As shown in Figure 25.2, paper, yard waste, and food waste are the principal biodegradable organic fractions. The biodegradability of these waste materials varies substantially as reported in Table 25.1. The issue of biodegradability is discussed further in the following section.

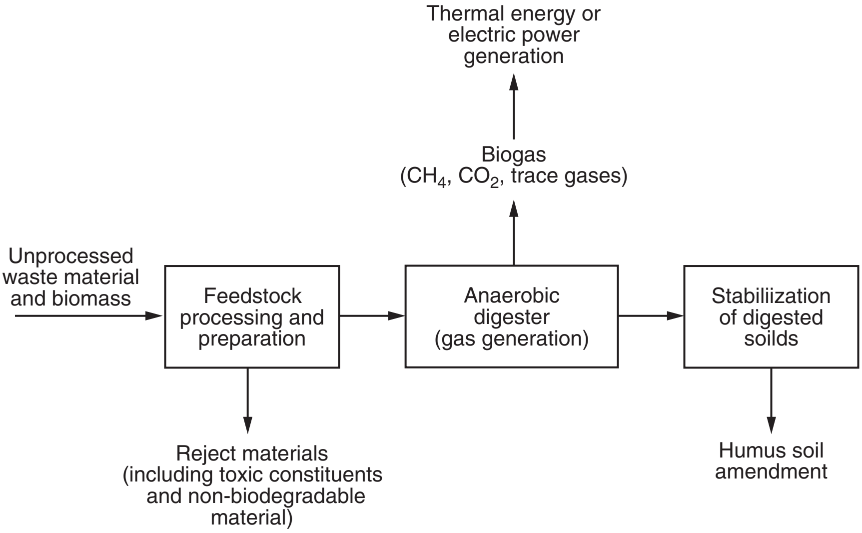

FIGURE 25.1 General flow diagram of bioenergy recovery system.

As illustrated in Figure 25.1, some waste material must be preprocessed to: (1) remove toxic constituents, (2) remove nonbiodegradable materials, and (3) prepare a balanced feedstock in terms of nutrient availability for methane recovery. Most livestock wastes and treatment plant sludge are relatively homogeneous, biologically active, and contain sufficient nutrients. Therefore, little or no preprocessing of feedstock may be needed. Also, because dairy and pig wastes contain a variety of anaerobic microorganisms, methane gas will be produced when proper conditions are provided. Thus, for the anaerobic digestion of organic wastes other than livestock wastes, the addition of dairy or pig manure is commonly used. The addition of livestock waste to activate a biological process is commonly known as "inoculation."

25.1.3 The Issue of Biodegradability

While each organic waste may contain a constant ultimate biodegradable fraction, practical biodegradability can be quite variable. Factors such as particle size, time, and environmental conditions

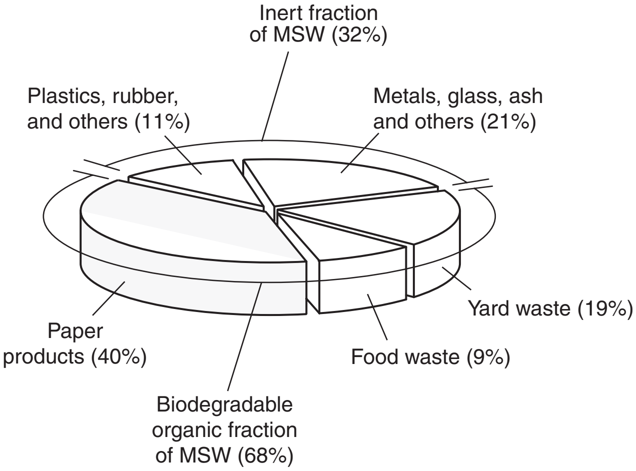

FIGURE 25.2 A typical MSW composition in the U.S.

TABLE 25.1 Weight Distribution and Biodegradability of the Organic Fraction of MSW Found in the U.S.

	Percent by Wet Weight		Biodegradability		
Component	Range	Typical	Low[a]	Medium[b]	High[c]
Paper					
Cardboard	3–10	10		X	
Magazines	2–8	6	X		
Newspaper	4–10	8	X		
Waxed cartoons	5–20	12			X
Other (mixed)	<1–5	3			X
Food waste	6–18	9			X
Yard wastes	5–20	15			X
Wood waste	1–4	1.5	X		

[a] Low-biodegradable materials are classified as having a biodegradability of less than 30%.
[b] Medium-biodegradable materials are classified as having a biodegradability of greater than 30% but lower than 75%.
[c] High-biodegradable materials are classified as having a biodegradability of greater than 75%.

(i.e., temperature, nutrient requirements, etc.) will influence the final outcome of biodegradation. For example, because favorable conditions do not exist in most landfills, the biodegradability estimated from analytical test will usually be greater than the actual biodegradation that occurs in landfills. For practical purposes, the discussion in this section deals with the biodegradability of the organic fraction of waste materials used in in-vessel anaerobic digestion processes. Substrate biodegradability is of special importance in an in-vessel anaerobic digestion processes, where the production of energy is of concern.[1,2]

25.1.3.1 Biodegradable Volatile Solids of an Organic Substrate

Dry organic substrates consist of volatile solids (VS) and ash. Taken together, these two components comprise the total solids (TS) of a substrate as illustrated in Figure 25.3. The fraction of ash typically depends on the nature of the organic substrate. VS is measured as loss on ignition. Only the biodegradable volatile solids (BVS) fraction of the VS has the potential for bioconversion largely because of the presence of refractory volatile solids (RVS) which, in most digester feedstocks, is mostly lignin. Lignin is a complex organic material which is difficult for anaerobic bacteria to degrade and normally requires a long period of time for complete degradation. It is clear from Figure 25.3 that organic substrates with high RVS and ash contents have a low biodegradability.

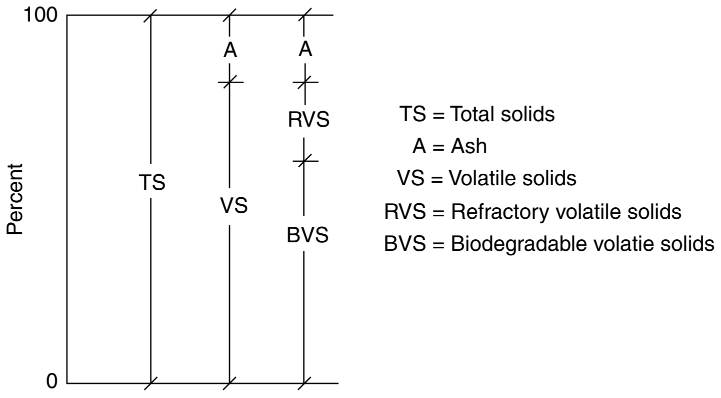

FIGURE 25.3 Characterization of a typical organic substrate.

The RVS in the organic fraction of MSW consists of the lignin content which is associated with cellulose in plant materials and thermoplastic materials. Lignin content of an unsorted organic fraction of MSW will fluctuate as the percentage of cellulose and thermoplastic materials will vary with season, socioeconomic conditions, and geographical locations. Knowing the BVS fraction of VS in the individual organic fractions of MSW will allow the biodegradability of any composite BOF/MSW to be estimated.

25.1.3.2 Methods to Estimate Biodegradability

Several methods can be used to estimate the BVS fraction of an organic substrate, including: (1) long-term batch digestion studies, (2) measurement of lignin content, and (3) chemostat studies. These methods are described briefly below.

25.1.3.2.1 Long-Term Batch Digestion

Batch digestion studies, designed to simulate a specific anaerobic digestion process, can be used to predict the biodegradable fraction of an organic substrate. One method involves graphical analysis of weight loss over time and is used commonly to predict the ultimate biodegradability of energy crops and agricultural wastes.[3] This method is based on a linear regression plot of the remaining VS concentration as the retention time approaches infinity. Regular weight measurements of the batch digester throughout the course of the study are required to apply this method.

An alternative method for determining the biodegradable fraction of an organic substrate, using batch digesters, is to determine and compare the initial and final dry masses. Initial measurements are made of the mass and the percent TS of active reactor mass of each mixture to be tested. Each mixture includes a percentage of seed, i.e., material taken from an active digester to provide suitable microorganisms. One batch mixture is always 100% seed. At the end of the batch study, the dry mass in each individual reactor is measured. The mass loss in each unit, corrected for seed biodegradation, is due to the conversion of the biodegradable portion of the substrate to biogas. The results of biodegradable fraction of municipal solid waste (BOF/MSW) based on long-term batch digestion studies are shown in Table 25.2.

25.1.3.2.2 Measurement of Lignin Content

An analytical method commonly used for determining the BVS fraction of an organic substrate is based on the measurement of the crude lignin content of the VS. Chandler et al.[1] correlated the biodegradability of various agricultural residues and newsprint, as determined by long-term batch digestion studies, with the lignin content of the substrate, as determined by sequential fiber analysis, developed by Robertson and Van Soest.[4] The following empirical relationship was developed to estimate the biodegradable fraction of an organic substrate from lignin test results:

$$\text{Biodegradable fraction} = 0.83\text{–}0.028 \times \text{LC} \qquad (25.1)$$

TABLE 25.2 Estimated Biodegradable Fraction of Organic Waste Components of MSW Based on Long-Term Batch Studies

	BVS Fraction, %VS		
Organic Substrate	Reactor 1	Reactor 2	Average
Newspaper	22.5	24.8	23.7
Office paper	83.5	81.8	82.7
Food waste	83.0	82.5	82.8
Yard waste	73.0	70.5	71.8
Mix blend[a]	70.5	69.5	69.8[b]

[a] Mixed blend consists of 19% newsprint, 53% office paper, 15% yard waste, and 13% food waste (dry basis).

[b] The value reported for mixed blend is based on the actual organic waste and not on the value that can be computed from each individual component.

TABLE 25.3 Estimated Biodegradable Fraction of Organic Waste Components of MSW Based on the Lignin Content

Lignin Content Range	Average BVS Fraction	
Organic Substrate	%VS	%VS[a]
Newspaper	20–23	22
Office paper	0.2–1	82
Yard waste	4–10	72
Food waste	0.1–0.7	82
Mixed blend[b]	4–7	67.6

[a] Computed using Equation 25.1.

[b] Mixed blend consists of 19% newsprint, 53% office paper, 15% yard waste, and 13% food waste (dry basis).

where the biodegradable fraction is expressed as a fraction of the VS, and LC the lignin content, expressed as a percentage of the VS. The results of biodegradable fraction for BOF/MSW based on the lignin content are shown in Table 25.3.

25.1.3.2.3 Chemostat Studies

The BVS fraction of an organic substrate can also be estimated using chemostat techniques. The true digestible organic matter (TDOM) technique, developed by animal scientists, is used to assess the digestibility of animal feeds.[5] The test involves the digestion of a sample in vitro in rumen fluid for 48 h. A second chemostat technique, the biochemical methane potential (BMP) assay, is used to characterize the BMP and biodegradability of many organic substrates.[6] In the BMP assay, the substrate biodegradability is determined by monitoring the cumulative methane production from a slurry sample which is incubated anaerobically (typically for 30 days at 35°C) in a chemically defined media and inocula.

The biodegradability of energy crops as estimated using the BMP assay tends to be 3%–10% higher than the corresponding BVS value as estimated using the TDOM technique.[7,8] The BMP assay appears to be more suitable for determining the ultimate biodegradability.

25.1.3.3 Biodegradability of Various Organic Waste Materials

The estimates of BVS, as a percentage of VS, of a typical organic fraction of MSW based on long-term batch studies, lignin content, and a pilot study are compared in Figure 25.4. As can be seen, the average BVS fractions calculated using either the lignin content or the long-term batch study are essentially the same. The BVS fraction obtained from the pilot study, using a complete-mix reactor and mass retention time (MRT) of 30 days, is about 83 and 81% of the estimated values obtained from the lignin content or the batch study, respectively. Similarly, Richards et al.[7,8] were able to remove only 83% of BVS of sorghum, using a thermophilic, high rate, high-solids reactor with a MRT of 45 days.

The values of biodegradable fraction for various organic substrates using different methods are compared in Table 25.4. It is important to note that the estimated BVS values based on field operations are normally about 80%–85% of the values estimated by chemostat studies. Thus, the use of BMP values would result in an overestimation of biogas production rate that can be achieved in actual practice. It is important to note that the complete removal of BVS as estimated from batch digestion and analytical or a chemostat method at a practical range of MRT (20–40) is not possible. For an in-vessel high-solids anaerobic digestion process, BVS can be defined as that fraction of VS that can be biodegraded under optimum environmental and nutritional conditions in a period of 20–40 days.

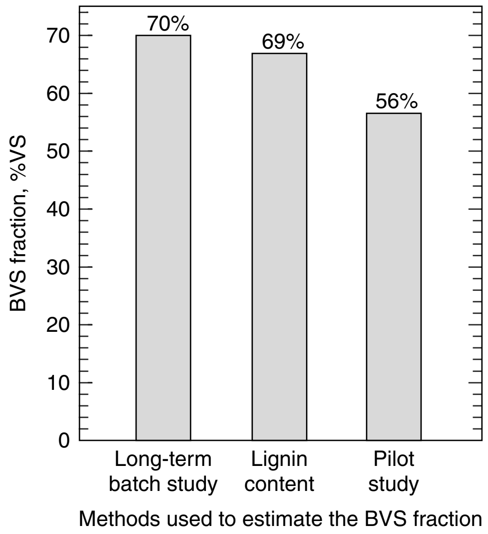

FIGURE 25.4 Comparison of the BVS fraction of a typical mixed BOF/MSW obtained using three methods of analysis.

25.1.3.4 Impact of BVS on Process Design and Performance

The common use of total or VS both in describing the organic loading rate and feedstock C/N ratio, and in estimating gas production from the BOF/MSW is misleading, as some of the organic compounds are low in biodegradability. The use of BVS instead allows meaningful comparisons to be made between the different anaerobic digestion processes reported in the literature. The impact of BVS on the organic loading rate, the computation of carbon to nitrogen (C/N) ratio, and the prediction of biogas production are discussed below.

Traditionally, the loading rates for biological processes have been based on the VS content of the substrate feedstock. When handling substrates with variable biodegradabilities, estimates of the methane production potential and digester performance cannot be made accurately using a VS loading rate. Loading rates based on the BVS fraction of the substrate should be used to estimate the conversion of organic wastes to methane. The BVS organic loading rate can be expressed as the input BVS mass per active reactor mass per day. The BVS mass of an organic substrate can be computed using total inflow VS mass multiplied by the BVS fraction of VS.

Customarily, the C/N ratio is determined based on the total dry mass of the organic matter and the corresponding percentage concentrations of carbon and nitrogen. This method of determining the C/N ratio may not be appropriate for the BOF/MSW because not all the organic carbon is biodegradable

TABLE 25.4 Biodegradability of Various Organic Substrate Using Batch Digestion, Chemostat, and Field Operation Methods

	Methods Used to Estimate Biodegradability				
	Average Value, %				
Substrate	Batch Digestion	TDOM	BMP	Field Operation[a]	Reference
Sorghum	60	79.1	82.0	72.6 (105)[b]	Richards et al. 1991a, 1991b[c]
Sorghum 1			90.9	75.0 (45)	Richards et al. 1991a
Sorghum 2			90.0	72.5 (29)	Richards et al. 1991a
Alpha-cellulose	81.6	90.6	99.8		Richards et al. 1991a
1:1 mix of sorghum/		70.8	87.6	90.7	Richards et al. 1991a
Alpha-cellulose BOF/MSW	69.8			57 (30)	Kayhanian and Tchobanoglous 1993a

[a] All field operations were conducted in a thermophilic, high-rate, high-solids reactor.

[b] Numbers in parentheses are nominal MRT value in days.

[c] Data for field operations were obtained from Richards et al.[8]

and/or available for biological decomposition. However, it appears that almost all the nitrogen in the organic material is available for conversion to ammonia via microbial metabolism.[9] Because the available nitrogen in the organic feedstock can be converted to ammonia, the C/N ratio should be based on the nitrogen content of the total organic mass and the carbon content of the BVS mass.[10]

A more accurate biogas volume production can be made from the BVS mass, rather than the TS or VS mass. However, not all the BVS mass computed using the lignin content or the results of long-term batch studies will be converted into biogas in field operation. For design purpose, a correction factor of about 0.82, derived from lignin test or long-term batch digestion, must be used when using the BVS mass as a basis for theoretical gas production. Computation of BVS fraction of the biodegradable fraction of MSW is illustrated in the following example calculation.

25.1.3.4.1 Example of BVS Calculation of MSW

Estimate the total BVS weight (mass) of a 100 tn./d MSW material recovery facility.

Use the following information:

1. Assume that the composition of a typical MSW waste stream given in Figure 25.2 is valid:
2. Typical characteristics of MSW sub-fractions:

Waste Material	Total Solids, %	Volatile Solids, %TS	Lignin Content
Yard Waste	40	88	6.43
Food Waste	30	90	0.36
Paper	94	98	9.29

25.1.3.4.2 Solution

1. Start from the typical composition of MSW and prepare a table:

	Weight, lb/d	
Waste Material	Wet Weight	Dry Weight
Yard waste	38,000	15,200
Food waste	18,000	5400
Paper	80,000	75,200
Metal	42,000	42,000
Plastic	22,000	22,000

[a]Calculated using the percent TS.

2. Calculate the biodegradable organic fraction of MSW being serviced by the sorting facility:

$$\text{BOF/MSW per day} = (0.68)(100\ \text{tn. MSW/d}) = 68\ \text{tn.}$$

3. Compute the total weight of BVS. To compute the BVS content of a substrate:

$$\text{VS weight} = \text{dry weight} \times \text{VS\%}$$

$$\text{BVS weight} = \text{VS weight} \times \text{BF}$$

where

$$BF = 0.83–(0.028 \times LC)$$

and

$$LC = \text{lignin content.}$$

4. Prepare a table for the values calculated:

Biodegradable Waste	Dry wt, lb/d	VS, % TS	VS wt, lb/d	BF, % VS	BVS wt, lb/d
Yard Waste	15,200	88	13,376	0.65	8694
Food waste	5400	90	4860	0.82	3985
Paper (mixed)	75,200	98	73,696	0.57	42,005
Total	95,800		91,932		54,684

[a]The values in this column are calculated as VS = dry weight × VS%.[b]The BF fraction is computed using Equation 25.1 and the lignin content or using the biodegradability value determined by a long-term batch study.[c]The values in this column are calculated as BVS = VS weight × BF.

25.1.3.4.3 Comments

It is important to note that the BVS weight is about 27% of the total wet weight of MSW, 40% of the total wet weight of BOF/MSW, and 60% of the total VS fraction of the TS.

25.1.4 Fundamentals of Anaerobic Digestion

The purpose of this section is to familiarize the reader with the basic microbiology related to an anaerobic digestion process. Topics discussed include: (1) an introduction to anaerobic bacteria, (2) nutrient requirements for the anaerobic bacteria, (3) physical and chemical parameters that affect anaerobic bacteria, (4) basic biochemical reaction in anaerobic digestion process, and (5) pathway of complex organic substrate in anaerobic digestion process.

25.1.4.1 Anaerobic Bacteria

Effective anaerobic degradation of complex organic waste is a result of the combined and coordinated metabolic activity of the digester microbial population. This population of microorganisms is composed of several major trophic groups. At present, as reported in Table 25.5, four different groups of anaerobic bacteria are recognizable. With respect to methane recovery, the anaerobic bacteria are generally grouped

TABLE 25.5 Four Major Groups of Anaerobic Bacteria and their Function

Bacterial Group	Function
Hydrolytic Bacteria	Catabolize saccharides, protein, lipids, and other minor chemical constituents of biomass
Hydrogen-producing acetogenic Bacteria	Catabolize certain fatty acids and neutral end products
Homoacetogenic Bacteria	Catabolize unicarbon compounds (e.g., H_2/CO_2 or HCOOH) or hydrolyze multi-carbon compounds to acetic acid
Methanogenic Bacteria	Catabolize acetate and one carbon compound to methane

Source: From Holland, K. T., Knapp, J. S., and Shoesmith, J. G., *Anaerobic Bacteria*, Chapman and Hall, New York, 1987.

TABLE 25.6 Morphological Characteristics of Methane Bacteria

Organism	Morphology	Length, m	PH Optimum	Electron Donor
Methanobacterium formicium	Rods, single pairs or chains	2–15		Hydrogen and formate
M. strain MOH	Rods, single pairs or chains	2–4		Hydrogen
M. arborphilicum	Rods, single pairs or chains	2–3.5	7.5–8	Hydrogen
M. strain AZ	Rods, single pairs or chains	2–3	6.8–7.2	Hydrogen
Methanosarcina barkeri	Sarcina	1.5–5	7	Methanol and hydrogen
Methanobacterium rominantium	Coccus chains	1–2 diameters	6.8–7.2	Hydrogen and formate
Methanococcus vanniellii	Coccus	0.5–4 diameters	7.4–9.2	Formate
Methanobacterium mobile	Rod			Hydrogen and formate
Methanobacterium thermoautotrophium	Rod	5–10		Hydrogen
Methanobacterium hungatii	Spiral rods	50		Hydrogen and formate

Source: From Holland, K. T., Knapp, J. S., and Shoesmith, J. G., *Anaerobic Bacteria*, Chapman and Hall, New York, 1987.

as: (1) hydrolytics (hydrolyzing bacteria), (2) acetogens (acid-forming bacteria), and (3) methanogens (methane-forming bacteria).

Methane bacteria are among the most strictly anaerobic microorganisms known and occur naturally in the rumen of cows, marshes, and brackish waters, as well as in wastewater treatment plant digesters. Methanogenic bacteria have been isolated from anaerobic digesters, together with other obligate anaerobes, such as the *Propionibacter*, *Butyrobactor*, and *Lactobacillus*. The true methane bacteria include the following identified genera: *Methanococcus*, *Methanobacterium*, *Methanosarcina*, *Methanospirillium*, and *Methanobacillus*. The main group of methane bacteria along with some of their morphological and growth characteristics are given in Table 25.6.

As reported in Table 25.6, methane bacteria are rod, cocci, or sarcinate in shape. As a group, methane bacteria are nearly always Gram-positive (a stain used to identify bacterial types) and usually not motile. Many methane bacteria are pleomorphic; that is, they exhibit variable morphology when viewed under the microscope, which makes their identification very difficult. Their length can vary between 2 and 15 μm. Nutritionally, the methanogenic bacteria are said to be cemolihoheterotrophic, which means that they can build up their cell structures from either carbonate or organic compounds. Morphologically, methanogens are a diverse group; however, physiologically, they are quite similar as all share the common metabolic capacity to produce methane. The methanogens are possibly the most important group of anaerobic bacteria. They have scientific significance in their exclusive and distinctive properties among the bacteria.

25.1.4.2 Nutrient Requirements for Anaerobic Bacteria

To operate a high-solids anaerobic digestion process at a commercial level, attention must be focused on process stability. Successful operational parameters have been established for the high-solids process studies conducted at the University of California at Davis.[11] However, in the anaerobic digestion of BOF/MSW, bacterial nutritional requirements have often been overlooked. Nutritional deficiencies may result in reactor instability and incomplete bioconversion of the organic substrates. When the anaerobic digestion process is applied to the biodegradable organic fraction of MSW, bacterial nutritional requirements must be addressed and nutrient supplementation may be required.[12,13]

Methanogenic bacteria have a variety of mineral nutrient requirements for robust growth.[14,15] For a proper bacterial metabolism, a variety of nutrients must be present in the substrate. The nutrient requirements for anaerobic bacteria can generally be categorized as macro- and micronutrient. For a stable anaerobic digestion process, these nutrients must be present in the substrate in the correct ratios

TABLE 25.7 Representative Feedstock Nutrient Concentrations Required for the Robust Anaerobic Bioconversion of BOF/MSW

Nutrient[a]	Unit	Average Value (Dry Basis)	
		Range	Typical
C/N[a]		20–30	25
C/P		150–300	180
C/K		40–100	70
Co	mg/kg	<1–5	2
Fe	mg/kg	100–5000	1000
Mo	mg/kg	<1–5	2
Ni	mg/kg	5–20	10
Se	mg/kg	0–0.05	0.03
W	mg/kg	0.05–1	0.1

[a] C/N, C/P, and C/K ratios are based on the biodegradable organic carbon and total nitrogen, phosphorus, and potassium.
Source: From Kayhanian, M. and Rich, D., *Biomass and Bioenergy*, 8, 433–444, 1995.

and concentrations. Based on studies conducted at UC Davis, it was found that typical BOF/MSW used as a feedstock for the anaerobic digestion process is deficient in many essential nutrients.[16] To overcome feedstock nutrient deficiencies, supplementary nutrients must be added to stimulate the digestion process. The range of nutrient concentrations needed to stimulate the anaerobic treatment of BOF/MSW for gas production is not well known. The nutrient values reported in Table 25.7 are based on three years of experience at the UC Davis high-solids biogasification project.

25.1.4.3 Physical and Chemical Parameters that Affect Anaerobic Bacteria

The alteration of several physical and chemical environmental parameters in anaerobic digesters can influence microbial populations and digester performance. Major environmental factors are summarized and shown in Table 25.8. Changing temperature from the mesophilic range to (i.e., below 45°C) the thermophilic range (i.e., above 55°C) increases organic mineralization and establishes a different species composition (i.e., thermophilic bacteria). Zeikus[17] found that thermophilic bacteria have a limited species composition, but they possess all the major nutritional categories and metabolize the same substrate as mesophilic bacteria. The ability to proliferate at growth temperature optima well above 60°C is associated with extremely thermo-stable macromolecules. As a consequence of growth at high temperatures and unique micromolecular properties, thermophilic bacteria can possess high metabolic rates, physically and chemically stable enzymes, and lower growth but higher end product yields than similar mesophilic species. Thermophilic digesters are generally digester substrates within shorter retention time than mesophilic digesters.

TABLE 25.8 Physical and Chemical Effectors of Bacterial Populations in Anaerobic Digesters

Parameter	Population Response	Influence of Methanogenesis
Temperature (e.g., change to 65°C from 35°C)	Enrichment of thermophilic	Increase
pH (e.g., change to pH 5 from pH 7)	Enrichment of acidophiles	Decrease
Organic substrate composition (e.g., change soluble substrate (glucose) for particulate (lignoglucose))	Enrichment of biopolymer decomposers	Decrease
Substrate feed rate (e.g., change from slow to high glucose feed)	Enrichment of hydrolytic bacteria	Decrease
Inorganic composition (e.g., addition of excess sulfate)	Enrichment of sulfate reducers	Decrease

Source: From Holland, K. T., Knapp, J. S., and Shoesmith, J. G., *Anaerobic Bacteria*, Chapman and Hall, New York, 1987.

Values of pH well below neutral are indicative of digester failure. The pH ranges for growth of many bacterial species inherent to anaerobic methane digester are not known and may vary considerably. Nevertheless, important hydrogen-producing (e.g., *C. thermocellum*) and hydrogen-consuming (e.g., *M. thermoautitrophicum*) anaerobes do not grow at pH value below 6. Digester imbalances that favor more rapid growth of non-methanogens (e.g., high feed rate or chemical composition of feed) can lead to low pH and inhabitation of methanogenesis. Low pH values favor proton reduction to hydrogen, but not hydrogen oxidation to protons. Thus, methanogens may not function at low pH because they employ oxidoreductases for hydrogen oxidation and establishment of proton gradients during the catabolism of one carbon compound and acetate.

The organic composition of digester wastes affects species composition and methane yield. Most notably, methane yields from municipal wastes and animal manures are often limited by polymeric lignin surrounding cellulose and retarding its fermentation. High molecular weight lignin is not metabolized significantly by anaerobic bacteria. However, methane yield from digestion of lignocellulosics can be enhanced greatly by physico-chemical pretreatment that separates lignin from cellulose and/or solubilize lignin into anaerobically digestible substrates. To accomplish lignin solubilization, an adaptation period is required to obtain an active microbial population from untreated waste digesters that metabolized soluble chemical hydrolysis products of lignin. The organic composition modification caused by waste pretreatment is considered to be associated with change in species compositional change.

The most significant parameter affecting methanogenesis during anaerobic digestion processes is sulfate inhabitation. The addition of high levels of sulfate to decomposing organic matter can result in nearly complete inhabitation of methane formation as a result of species compositional change. The basis for this inhabitation is that carbon and electron flow during organic mineralization is diverted from methane formation to hydrogen sulfide production. The response of sulfide on many methanogens is concentration dependent. Sulfide is required by many methanogens as a sulfur source for growth. The addition of low sulfide concentrations often stimulates mixed culture methanogenesis, whereas addition of high concentrations can be inhibitory.

25.1.4.4 Pathway of a Complex Organic Substrate in Anaerobic Digestion Process

A generalized scheme for the anaerobic digestion of complex organic substrate is shown in Figure 25.5. Anaerobic digestion is generally considered to take place in three distinct stages. The three stages have been described as: (1) hydrolysis, (2) acetogenesis, and (3) methanogenesis. Each of the three stages has distinct bacterial groups and chemical reactions, and it proceeds in an assembly-line fashion.[18]

As depicted in Figure 25.5, the overall process begins with the hydrolysis of complex organic compounds into soluble components. Next, the acid-forming bacteria ferment the soluble components into a group of extracellular intermediates, including various volatile fatty acids (VFA's), hydrogen (H_2), and carbon dioxide (CO_2). The concentrations of the intermediate acids are usually small in proportion to their production and degradation rates, and they are quickly transformed to methanogenic substrates, including acetate, methanol, and formate. These products are then converted to methane by the methanogenic bacteria.

Methane bacteria can only use limited range of substrates for growth and energy production. During anaerobic digestion, a varied mixture of complex compounds is converted to a very narrow range of simple compounds, mainly methane and carbon dioxide. The ecology of the system is much more complicated and involves an interacting succession of microbes which influences each others' growth and metabolism. Nearly all anaerobic bacteria can use hydrogen and carbon dioxide, most can use formate, a few acetate, and fewer still methanol and methylamines. However, in the mixed population and with many organisms, the range of fermentation products is restricted. The restriction is due to the phenomenon of interspecies hydrogen transfer by which methanogens utilize hydrogen

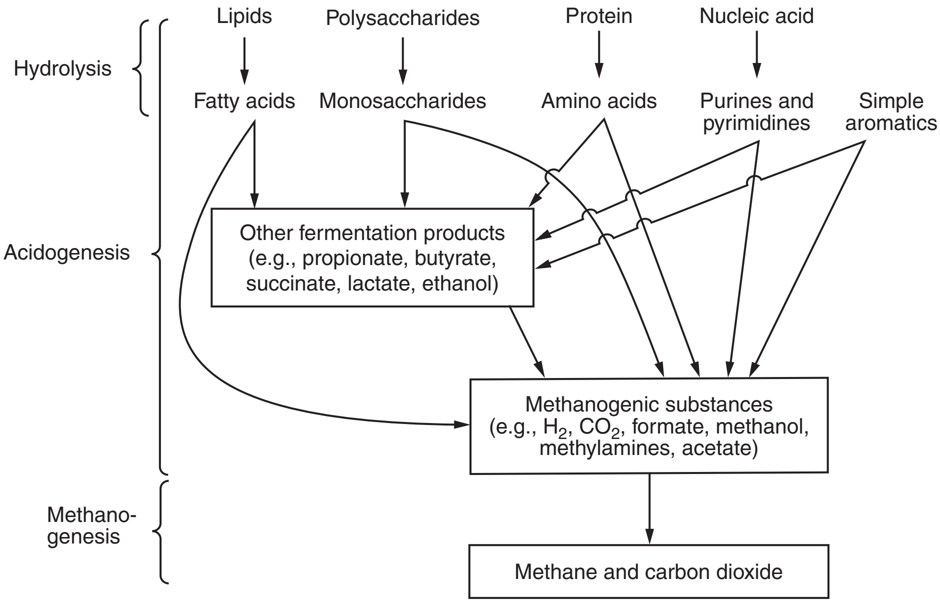

FIGURE 25.5 Stages of anaerobic digestion. (From Tchobanoglous, G., Theisen, H., and Vigil, S. A., *Integrated Solid Waste Management—Engineering Principles and Management Issues*, McGraw-Hill Book Company, New York, 1993.)

and thus benefit other organisms. Hydrogen removal is helpful as it allows some organisms to dispose of more electrons via hydrogen rather than via the production of more reduced carbon compounds, such as ethanol or butyrate. In general, fatty acids are the "key" intermediate products of the anaerobic fermentation of organic compounds prior to methane formation. Acetate is by far the predominant fatty acid in normally operated systems, being responsible for about 70% of the fatty acid present. The VFA measurements are usually expressed in mg/l, therefore, as being acetate equivalent.

25.1.4.5 Basic Biochemical Reaction in Anaerobic Digestion Process

The anaerobic bacteria described in previous sections are responsible for biochemical transformation of a wide variety of waste materials. These transformations are involved in the breakdown of complex polymers, such as cellulose, fats, and proteins, to long- and short-chain fatty acids and finally methane, carbon dioxide, and water. The basic biochemical reactions affected by anaerobic microbial population are oxidation/reduction reactions, where a number of organic compounds are oxidized by the removal of hydrogen. Carbon dioxide, is thereby, reduced in providing an oxidant for the methane bacteria. The hydrogen produced can be replaced by some of the organic acids and alcohols as direct reductants of carbon dioxide. The basic biochemical reactions utilizing hydrogen, carbon dioxide, carbon monoxide, alcohols, organic acids, methylamines, and other protein derivative compounds as a substrate are summarized in the energy-yielding equations given in Table 25.9.

The general anaerobic transformation of the biodegradable organic fraction of MSW can be described by the following equation:[19]

$$\begin{aligned}\text{Organic matter} + H_2O + \text{nutrients} &\rightarrow \text{new cells} + \text{resistant organic matter} + CO_2 \\ &+ CH_4 + NH_3 + H_2S + \text{heat}\end{aligned} \tag{25.2}$$

TABLE 25.9 Summary of Most Common Biochemical Reactions in Anaerobic Digestion Process

Substrate	Biochemical Reactions
Hydrogen and carbon dioxide	$4H_2+CO_2\rightarrow CH_4+2H_2O$
Carbon monoxide	$4CO+2H_2O\rightarrow CH_4+3CO_2$
Alcohols	$4CH_3OH\rightarrow 3CH_4+CO_2+2H_2O$ $CH_3OH+H_2\rightarrow CH_4+H_2O$ $4HCOO^- +2H^+\rightarrow CH_4+CO_2+2HCO_3^-$
Fatty acids	$HCOO^- +3H_2+H^+\rightarrow CH_4+2H_2O$ $CH_3COO^- +H_2O\rightarrow CH_4+HCO_3^-$ $4CH_2NH2+2H_2O+4H^+\rightarrow 3CH_4+CO_2+4NH_4^+$
Methylamines and other protein derivative compounds	$2(CH3)_2NH +2H_2O+2H^+\rightarrow 3CH_4+CO_2+2NH_4^+$ $4(CH_3)_3N+6H_2O+4H^+\rightarrow 9CH_4+3CO_2+4NH_4^+$ $2CH_3CH_2-N(CH_3)_2+2H_2O\rightarrow 3CH_4+CO_2+2CH_3CH_2NH_2$

For practical purposes, the overall conversion of the organic fraction of solid waste to methane, carbon dioxide, and ammonia can be represented by the following equation:[19]

$$C_aH_bO_cN_d \rightarrow nC_wH_xO_yN_z + mCH_4 + sCO_2 + rH_2O + (d–nx)NH_3 \tag{25.3}$$

where $s=a-nw-m$, $r=c-ny-2s$

The terms $C_aH_bO_cN_d$ and $C_wH_xO_yN_z$ are used to represent (on a molar basis) the composition of the organic material present at the start and the end of the process, respectively. If it is assumed that the organic wastes are stabilized completely, then the corresponding expression is

$$\begin{aligned} C_aH_bO_cN_d + \left(\frac{4a-b-2c+3d}{4}\right)H_2O \rightarrow \left(\frac{4a+b-2c-3d}{8}\right)CH_4 \\ + \left(\frac{4a-b+2c+3d}{8}\right)CO_2 + dNH_3 \end{aligned} \tag{25.4}$$

The above relationship can be used to estimate the theoretical biogas volume and composition. Estimation of the amount of gas produced by the complete anaerobic stabilization of the biodegradable VS fraction of MSW is illustrated in the following example calculation.

25.1.4.5.1 Estimation of Gas Production

Estimate the total theoretical amount of gas that could be produced from MSW under anaerobic conditions in an in-vessel anaerobic digestion process. Assume that 78% by weight of the MSW is organic material, including moisture. Further assume that the moisture content is 20%, the VS are 83.5% of the total organic solids, the BVS are 75% of the VS, and only 90% of the biodegradable VS will be converted to biogas. The overall chemical formula for the biodegradable organic material is $C_{60}H_{95}O_{38}N$.

25.1.4.5.2 Solution

1. Determine the BVS

$$\text{BVS} = 78 \times (1-0.2) \times 0.835 \times 0.75 = 39.1 \text{ lb}$$

2. Determine the total amount of BVS that will be converted to gas

$$\text{BVS}_{\text{gas}} = 39.1 \times 0.9 = 35.2$$

3. Using the chemical formula $C_{60}H_{95}O_{38}N$, estimate the amount of methane and carbon dioxide that can be produced using Equation 25.4.

$$C_aH_bO_cN_d + \left(\tfrac{4a-b-2c-3d}{4}\right)H_2O \rightarrow \left(\tfrac{4a+b-2c-3d}{8}\right)CH_4 + \left(\tfrac{4a-b+2c+3d}{8}\right)CO_2 + dNH_3$$

For the given chemical formula, $a=60 \quad b=95 \quad c=38 \quad d=1$
The resulting equation is

$$\underset{(1437)}{C_{60}H_{94.3}O_{37.8}N} + \underset{(324)}{18.28H_2O} \rightarrow \underset{(512)}{31.96CH_4} + \underset{(1232)}{28CO_2} + \underset{(17)}{HN_3}$$

4. Determine the weight of methane and carbon dioxide from the equation derived in step 3 and the data from step 2.

$$\text{Methane} = \frac{512}{1437}(35.2\ \text{lb}) = 12.5\ \text{lb}(5.7\ \text{kg})$$

$$\text{Carbondioxide} = \frac{1232}{1437}(35.2\ \text{lb}) = 30.2\ \text{lb}(13.7\ \text{kg})$$

5. Convert the weight of gases, determined in step 4, to volume, assuming that the densities of methane and carbon dioxide are 0.0448 and 0.1235 lb/ft.^{3}, respectively.

$$\text{Methane} = \frac{12.5\ \text{lb}}{0.0448\ \text{lb/ft.}^3} = 279\ \text{ft.}^3(7.9\ \text{m}^3)$$

$$\text{Carbondioxide} = \frac{30.2\ \text{lb}}{0.1235\ \text{lb/ft.}^3} = 244\ \text{ft.}^3(6.9\ \text{m}^3)$$

6. Determine the percentage composition of the resulting gas mixture using the gas volume determined in step 5

$$\text{Methane}(\%) = [279/(279+244)] \times 100 = 53.35\%$$

$$\text{Carbondioxide}(\%) = 100 - 53.35\% = 46.65\%$$

7. Determine the total theoretical amount of gas generated per unit weight of dry BVS, as determined in step 1 and per ton of MSW

$$((279+244)/39.1) = 13.4\ \text{ft.}^3/\text{lb BVS}(1.48\ \text{m}^3/\text{kg BVS})$$

$$\text{Biogas/ton of MSW} = 13.4\ \text{ft.}^3/\text{lb} \times 2000 \times 0.78 \times 0.8 \times 0.835 \times 0.75 = 10.470$$

25.1.4.5.3 Comment

The theoretical gas production value determined above has been achieved with the high-solids anaerobic decomposition process (see Section 24.1.6).

25.1.5 Monitoring of the Anaerobic Digestion Process

Although the high-solids anaerobic digestion process is generally robust, care must be taken to ensure balanced operation. To aid the prevention of unbalanced digester operation and to prevent digester failure, proper methods of monitoring the high-solids anaerobic digestion process are described, and possible operational problems are identified along with suggested remedial actions to be taken when these problems arise.

25.1.5.1 Balanced Digestion

A balanced digester is one in which anaerobic digestion proceeds with a minimum of control. Balanced operation means that the environmental parameters of the system remain within their optimum range, with only occasional fluctuations. When an imbalance does occur, the two main problems are: (1) identifying the beginning of an unbalanced condition and (2) identifying the cause of the imbalance. Unfortunately, there is no single parameter that will always indicate the commencement of an unhealthy anaerobic process. The parameters shown in Table 25.10 must all be monitored daily. None of these parameters can be used individually as a positive indicator of the development of digester imbalance.

The most immediate indication of impending operational problems is a significant decrease in the rate of gas production. If the growth of the microorganisms is being inhibited by one or more factors, it will be reflected in the total gas production. However, a decrease in the gas production rate may also be caused by a decrease in either the digester temperature or the rate at which the feed material is being added to the digester.

The most significant single indicator of a digester problem is a gradual decrease in pH. In an operating system, a decrease in pH is associated with an increase in organic acid concentration. Measurement of the increase in organic acids is also a good control parameter; however, proper laboratory facilities, equipment, and trained personnel are required to monitor this and most of the other control parameters affecting the anaerobic process. Gas production rate and pH are simple, quick measurements and are performed easily.

25.1.5.2 Common Problems and Solutions to Stabilize Digester Operation

In general, there are five major problems associated with the anaerobic digestion process: (1) increase in TS concentration, (2) organic overloading, (3) toxic overloading, (4) free ammonia toxicity, and (5) nutrient deficiency. Possible cures for these problems are summarized in Table 25.11.

25.1.6 Reactor Types Used for Anaerobic Digestion

In the past 50 years, a wide variety of in-vessel anaerobic digestion processes and reactors have been used for both waste stabilization and energy recovery. The anaerobic digestion is used most commonly in wastewater treatment plants for sludge stabilization with and without methane gas recovery plants.[20] In-vessel digesters have also been used by dairy and hog farmers to stabilize their waste as well as to produce methane gas for the production of electrical power to offset their power consumption during

TABLE 25.10 Indicators of Unbalanced Operation of the Anaerobic Digestion Process

Parameters	Warning Condition
Ammonia concentration	Increases
Percent of CH_4 in biogas	Decreases
Percent of CO_2 in biogas	Increases
Reactor pH	Decreases
Total gas production	Decreases
VFA concentration	Increases
Waste stabilization	Decreases

TABLE 25.11 Summary of the Most Common Problems Associated with the Anaerobic Digestion Process and Suggested Actions to Cure the Problems

Major Problem	Suggested Action
Free ammonia toxicity	1. Start feeding with an organic waste of higher C/N ratio 2. Dilute the active reactor mass with fresh water
Nutrient deficiency	1. Add chemical nutrient into the reactor 2. Add organic materials rich in the needed nutrients
Organic overloading	1. Do not feed 2. Add strong base to neutralize acids 3. Resume feeding at lower organic loading rate when pH reaches at least 6.8
Total solids build-up	1. Add water
Toxic overloading	1. Identify and remove the toxic element from the feedstock 2. If the population of methanogens are reduced (CH_4 concentration decreased), add proper methanogen seed 3. If pH decreases below 6.8, add strong base to neutralize acids 4. Resume feeding at lower organic loading rate when pH reaches at least 6.8

pick hours and on annual basis.[21,22] The principal types of in-vessel anaerobic digestion reactor designs that can be used for methane recovery and energy production are shown in Figure 25.6 and described below briefly.

25.1.6.1 Batch Reactor

A *batch reactor* is fed once, and then the biotransformation is allowed to proceed until completion before any material is added or removed. The evolution of compounds in the reactor can be monitored and a similar level of decomposition can be achieved by all the material in the reactor at one time. Additionally, the systems are generally simple, with less support equipment than continuous fed reactors (see below). Batch processes are necessary when the biotransformation being performed requires a long reaction time. Solids which are treated undiluted are often treated with batch reactors.

Usually, batch processes require more operator labor, for feeding and unloading, than continuous feed processes, and especially so for liquids and slurries, which are easily piped and pumped. For solids, the material handling needs are more similar for the two processes. Storage facilities are needed to contain waste received between batches. The need for storage can be inconvenient for large-scale, continuously produced wastes. A simplified diagram of a batch digestion is shown in Figure 25.6a.

25.1.6.2 Complete-Mix Continuous Flow Reactor

A reactor to which a waste stream is fed and a treated effluent stream is withdrawn continuously is known as a *continuous flow reactor*. Most municipal wastewater sludge treatment processes are continuous feed processes, as municipal sludge is produced continually. A process can be designed to fit the expected maximum inflow rate, although fluctuations in flow rate and process upsets may interfere with operation. If alternate storage is not available, discharge of untreated or partially treated wastes can occur.

The average residence time of material in a continuous feed reactor can be determined using the following equation:

$$t = V/Q \tag{25.5}$$

where t = residence time, V = reactor volume, and Q = flow rate (vol/time).

Reactors that are fed liquids or slurries continuously require less operator labor than batch reactors. Because storage space is not necessary to contain continuously produced wastes between batches, continuous feed processes are used commonly for industrial or municipal wastes. There are two types of

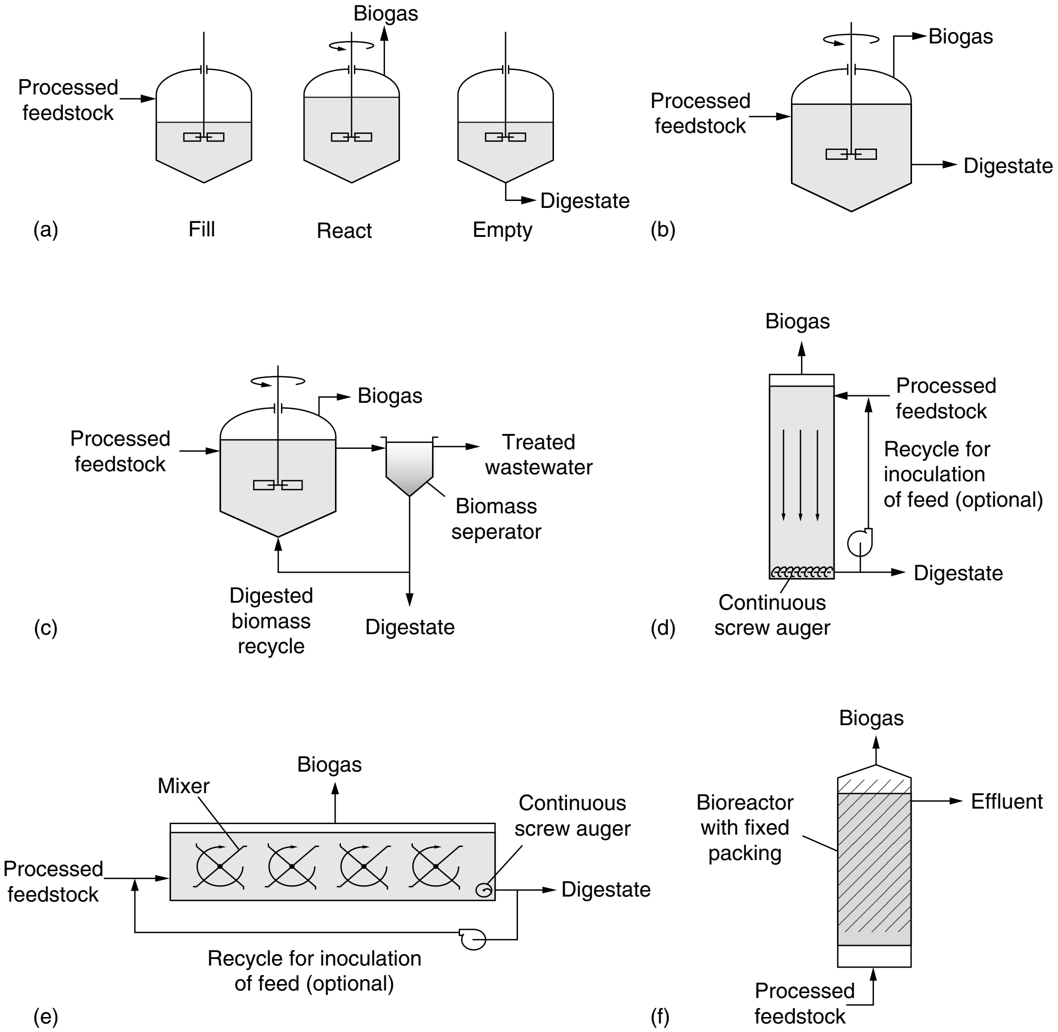

FIGURE 25.6 Typical reactor types used for anaerobic digestion: (a) batch reactor, (b) complete-mix continuous flow tractor, (c) anaerobic contact reactor, (d) vertical plug-flow reactor, (e) horizontal plug-flow reactor, and (f) attached growth reactor.

reactor which are intermediate between continuous feed and batch processes. A reactor which is fed once a day is a semi-continuous feed reactor. Also, a reactor which is fed continually, but only emptied when waste stabilization has been achieved, is a semi-batch reactor.

In a *complete-mix reactor*, the reactor contents are blended to homogeneity with a mixing device. The effluent leaving the reactor is exactly the same as the material in every part of the reactor. If fed continuously, the input waste is considered to be immediately mixed completely with the reactor contents. These reactors can also be described as well-mixed or as continuous stirred-tank reactors (CSTRs). A simplified diagram of a complete-mix reactor is shown in Figure 25.6b. One advantage of a complete-mix process is that fluctuations in feed concentration or composition are diluted into the larger reactor mass. Because of this dilution and the concentration of waste nutrient determines the rate of waste decomposition, complete-mix reactors have a slower decomposition rate.

25.1.6.3 Anaerobic Contact Reactor

The anaerobic contact process (ACP) is used to overcome the disadvantages of the complete-mix reactor without recycle. To enhance the rate of treatment, biomass is separated from the effluent and returned to the reactor. Biomass recycle can be used to reduce the reactor size and cost. A simplified ACP is shown in Figure 25.6c. Hydraulic retention times as low as a half-day have been achieved resulting in a significant reduction in plant size. ACP has been applied successfully for the treatment of meat-packing waste, where a retention time of several hours was measured. ACP is also used for the treatment of a high-strength waste material and is usually operated under low solids (TS less than 8%).

25.1.6.4 Plug-Flow Reactor

All *plug-flow reactors* are continuously or semi-continuously fed. In a plug-flow reactor, material passes through, ideally, without interacting with the material fed in before or after it. These reactors can be thought of as tubes through which independent batches of reacting material pass. The reactor can be either vertical or horizontal flow as shown in Figure 25.6d and e, respectively.

The retention time for a plug-flow reactor is the length of time it takes a mass introduced at the beginning of the reactor to pass through and be removed from the other end (see also Equation 25.5). Most horizontal plug-flow digesters are operated under low solids (usually with TS of less than 10%). Because the incoming, high-nutrient wastes are not diluted into the rest of the digester contents, the plug-flow digesters are more susceptible to system upsets due to sudden increases in waste concentration, called shock loadings. Fortunately, a certain degree of back mixing is unavoidable throughout the reactor due to longitudinal dispersion.

25.1.6.5 Anaerobic Attached Growth Reactor

Anaerobic attached growth reactors are used to prevent the depletion of the bacterial population within the reactor and, thus, improve digester efficiency. The retention of bacteria within the reactor is achieved by introducing some type of packing material on which the bacteria can grow. Various materials such as stone granules, wood chips, and plastic materials of various shapes and sizes have been used as packing material. The bacteria adhering to the filter particles bring about the treatment of the liquid as it passes through the reactor. Excess biomass dies and/or sloughs off and passes out as sludge. The anaerobic filtration process is usually used for the treatment of a high-strength waste material and usually operated under low solids (TS less than 8%). A simplified anaerobic filtration process is shown in Figure 25.6f.

25.1.6.6 Reactors with Recycle Flow

Often it is advantageous to recycle and mix effluent from an anaerobic reactor (digestate) with the inflowing waste stream (see Figure 25.6c, d, and e). Recycling is especially advantageous when it is necessary to inoculate the incoming waste with bacteria that have acclimated to the system. Recycling of biomass can also be used to increase average residence time in the reactor and to dilute high-concentration wastes. Recycling a portion of the biomass can also be used for process control, allowing the reactor to respond to fluctuations in the waste stream. Recycling systems, however, add costs, both capital and operational, to a system. Hence, unless it is necessary, the use of a simpler, *unrecycled* system is typically favored.

25.1.7 Modes of Operation for Anaerobic Digestion

To design an in-vessel anaerobic digestion, several parameters must be specified. These parameters may influence the physical characteristics of the reactor, the mode of operation, and the performance of a digestion system. Several modes of operation are discussed below.

25.1.7.1 Low-Solids Digestion

Anaerobic digestion systems for municipal wastewater operate under *low-solids* conditions; that is, the concentration of solids in the waste substrate is typically less than 10%. This mode of operation is appropriate because both municipal wastewater and the sludge collected for disposal from aerobic wastewater treatment processes are intrinsically low solids. The waste substrate in a low-solids system can be pumped and piped easily as it behaves like water. A low-solids system is also more able to handle feed composition fluctuations and higher ammonia levels, because the large volume of water serves to dilute the incoming waste compounds. Dilution of waste compounds also means dilution of nutrients, unfortunately, so that low-solids digestions can require more retention time if the nutrient level is too low. Also, the high dilution means that larger-sized tanks are required to accommodate wastes.

It is possible to digest substrates other than wastewater treatment sludge, however, and many of these waste substrates have a higher solids content. *High-solids* anaerobic digestion has recently been developed to accommodate these wastes. Originally developed to dispose of agricultural wastes, particularly manures, high-solids anaerobic digestion can be used to degrade food industry wastes, the biodegradable organic fraction of municipal solid waste (BOF/MSW), agricultural and forestry residues, and other high-solids wastes.

25.1.7.2 High-Solids Digestion

High-solids anaerobic digestion operates at solids contents from 20 to 32%. Typically, high-solids wastes, such as BOF/MSW, must be mixed with water or a low-solids waste, such as wastewater treatment sludge, to dilute the solids content to within the operating range. A high-solids system can operate with tanks that are up to 75% smaller than a low-solids system, for the same dry weight of waste. Because the nutrient in a high-solids reactor is more concentrated, the conversion rate is higher. Additionally, the high-solids process produces an end product that requires less dewatering to convert it into a landfillable waste or a usable compost material. High-solids anaerobic digestion systems are, however, more sensitive to micronutrient deficiencies and toxic inhibition, since there is more mass to digest and is diluted with less moisture. Especially, thermophilic systems are critically dependent on the maintenance of a proper carbon-to-nitrogen ratio, as explained below.

25.1.7.3 Thermophilic Digestion

Process in which the waste substrate is heated to between 120 and 135°F is characterized as *thermophilic*. Although heating the reactor adds additional equipment and energy costs, thermophilic process has a higher reaction rates as compared with ambient processes. Because bacterial metabolism is greater at the higher temperatures, a wider range of bacteria can colonize the reactor. Due to a decrease in water solubilization with increased temperature, thermophilic processes can be more vulnerable to inhibition effects due to the presence of some soluble compounds. Thermophilic methanogenic systems, for example, are more sensitive to high ammonia concentrations than are similar mesophilic systems.

25.1.7.4 Mesophilic Digestion

Processes in which the waste substrate has a temperature of between 68 and 98°F are characterized as *mesophilic*. Often no heating equipment at all is used. Although less costly than thermophilic systems, the time necessary for bioconversion may be significantly longer. If heating equipment is not used, the efficiency of the process will also depend on the weather.

25.1.7.5 Two-Stage Digestion

As discussed in previous sections, anaerobic digestion is principally carried out by three separate microbial populations under three distinct and interconnected stages. In the second stage of the digestion process, a group of bacteria convert soluble wastes to organic acids and, finally, at third stage methane bacteria convert organic acids to methane gas. Acid-forming and methane bacteria are distinct from each other in several features. These features include: their physiology, nutrient requirements, growth capabilities, and sensitivity to environmental stress. A single-stage digester can be most efficient only when a compromise is achieved between the relatively fast growing acid bacteria and the slower, more sensitive methane generators.

A two-stage digester (see Figure 25.7) is designed to isolate the acid and methane bacteria into separate reactors and optimize each environment for maximum reaction rate. Distinct features

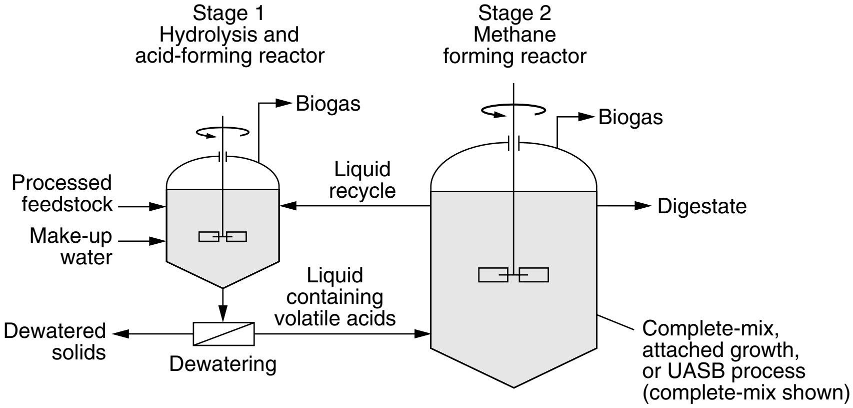

FIGURE 25.7 Two-stage anaerobic digestion.

of two-stage reactor are overall greater efficiency and system stability, and substantial reductions in total reactor volume. Several methods can be used to separate the non-methanogenic and methanogenic bacteria:

1. Various inhibitors may be introduced into the acid digester to prevent methanogenesis:
   a. adding chloroform
   b. adding carbon tetrachloride
   c. limiting oxygenation
   d. adjusting redox potential
2. Dialysis of methane bacteria by filtering the acids.
3. Adjusting the dilution rate and recycling of cell mass to each phase.

25.1.7.6 Co-Digestion of Wastewater Treatment Sludge and BOF/MSW

The co-digestion of WWTPS and BOF/MSW have been investigated by numerous researchers.[23–28] Most of these early studies concluded that high-quality source separated MSW could be digested without nutrient supplementation up to organic loading rates of about 2.6 kg VS/m^{3}d. They also reported that under conditions of nutrient addition, gas production could be enhanced and a more stable process could be achieved. Other studies conducted by Rivard et al.[12,13]; Babbitt et al.[29] and Cecchi et al.[30] confirmed the stabilizing effect of sludge to the digestion of MSW, with sludge comprising between 8 and 20% of feedstock VS.

One large-scale co-digestion of MSW and wastewater sludge has been demonstrated in the U.S. by the REFCOM project in Tampa, Florida.[31] The REFCOM system was based on a conventional low-solids digester design and operated as part of a total resource recovery process. The successful operation of the REFCOM process for mixed MSW at a rate of 50 tn./d or greater has confirmed the technical feasibility of the anaerobic digestion process. Reliable gas production was achieved in this facility for more than a year, indicating that MSW with wastewater sludge as a co-substrate can support an anaerobic biological conversion process.

Most co-digestion studies conducted prior to 1990 were low-solids processes, typically at a TS of 4%–8%. Only recently has the high-solids anaerobic digestion process been utilized for the co-digestion of MSW and WWTPS.[12,13,32] In these high-solids digestion studies, the sludge was mainly used to provide sufficient nutrients for microbial growth and metabolism. Nearly 10 years ago, the technical feasibility of the anaerobic composting process was demonstrated for co-management of BOF/MSW and WWTPS at UC Davis, as described below.[33]

TABLE 25.12 Comparison of Aerobic and Anaerobic Composting Processes

Characteristic	Aerobic Process	Anaerobic Process
Energy use	Net energy consumer	Net energy producer
End products	Humus, CO_2, H_2O	Sludge, CO_2, CH_4
Volume reduction	Up to 50%	Up to 50%
Processing time	21–30 days	20–40 days
Primary goal	Volume reduction	Energy production
Secondary goal	Compost production, waste stabilization	Volume reduction, waste stabilization

Source: From Kayhanian, M. and Tchobanoglous, G. 1993b. *Environmental Technology*, 14, 815–829.

25.1.7.7 Two-Stage Anaerobic Composting

In anaerobic composting, the focus is twofold: (1) production of methane as a source of energy and (2) complete waste stabilization to produce humus like material. Anaerobic digestion normally occurs at much higher solids content (e.g., 25%–32%). When a high-solids anaerobic digestion process is combined with a second stage aerobic biodryer, the two-stage process is termed "anaerobic composting".[34,35] The principal differences between the conventional aerobic and anaerobic composting processes are summarized in Table 25.12. The process flow diagram, physical characteristics of the reactors, and the energy recovery and volume reduction achieved are described below.

25.1.7.7.1 Process Flow Diagram

The process flow diagram for the anaerobic composting process studied at the University of California, Davis (UC Davis) is illustrated in Figure 25.8. As shown in Figure 25.8, the process involves two separate stages. The first stage of the two-stage process involves the high-solids anaerobic digestion of the biodegradable organic fraction of MSW to produce a gas, composed principally of CH_4 and CO_2, and digested solids. The second stage of the two-stage process is used to decrease the moisture content of the anaerobically digested solids. Typically, the solids content of the digested solids is increased from 25 to about 65%. Because the second stage aerobic process is used to dry the digested solids, the term *biodryer* is also used to describe the process. The physical and operational characteristics of the pilot anaerobic composting facilities used at UC Davis are briefly described below.

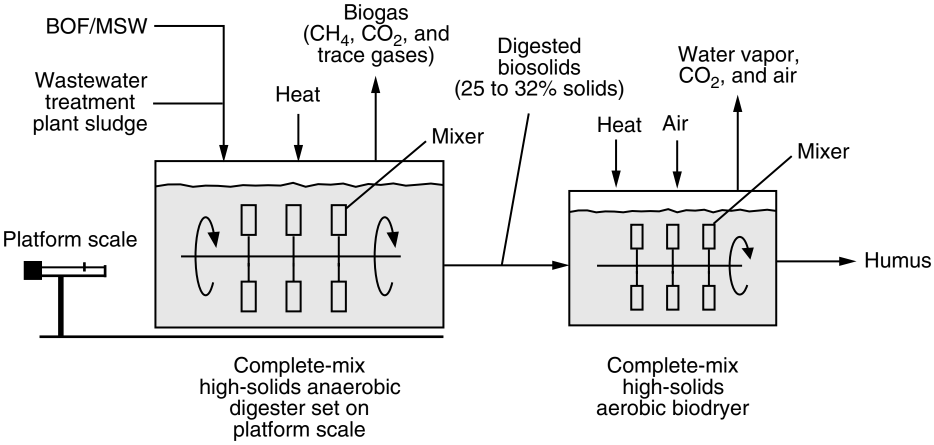

FIGURE 25.8 Flow diagram of the two-stage anaerobic composting process studied at UC Davis. The platform scale was used to obtain data for the preparation of materials mass balances.

TABLE 25.13 Summary of the Physical Characteristics of the UC Davis Pilot-Scale High-Solids Anaerobic Digestion/Aerobic Biodrying Processing Units

Item	Unit	Description/Value
Anaerobic digester		
Reactor type		Complete-mix
Mixing mechanism		Mechanical
Heating mechanism		Thermal blanket
Total reactor volume	l	2548
Volume of active reactor solids	l	1900
Aerobic biodrying unit		
Reactor type		Complete-mix
Mixing mechanism		Mechanical
Heating mechanism		Thermal blanket
Total rector volume	l	850
Volume of active reactor solids	l	765

Source: From Kayhanian, M., Lindenauer, K., Hardy, S., and Tchobanoglous, G., *BioCycle*, 32, 48–64, 1991.

25.1.7.7.2 Physical Characteristics

The physical characteristics of the pilot-scale anaerobic composting facilities are summarized in Table 25.14. As reported in Table 25.13, both the anaerobic digester and the biodryer are designed to operate as complete-mix reactors. Additionally, both units are equipped with thermal blankets and individual control panels so that they may be operated either manually or automatically. Further information on the UC Davis pilot-scale anaerobic digestion process design and performance can be obtained from Kayhanian and Tchobanoglous[10]; Kayhanian and Rich[33]; Kayhanian et al.[35]; Kayhanian[36]; Kayhanian and Hardy,[37] and Kayhanian et al.[38]

25.1.7.7.3 Energy Recovery and Volume Reduction

The results of the UC Davis co-digestion pilot study based on energy recovery and volume reduction are illustrated by the following two example calculations.

25.1.7.7.4 Energy Recovery—Example Calculation

Computation of the energy value that can be produced from the digestion of a 1000 tn./d MSW processing facility using primary sludge as a co-substrate.

1. Compute total organic mass
   Assume 75% of total mass is organic
   Organic mass $= 0.75 \times 1000 = 750$ tn./d
2. Compute total dry organic mass
   Assume 20% of organic mass is moisture
   Dry organic mass $= 750 \times 0.8 = 600$ tn./d.
3. Compute the biodegradable VS mass in MSW
   Assume 90% of dry organic mass is VS and
   70% of the VS mass is biodegradable
   BVS mass $= 600 \times 0.9 \times 0.7 = 378$ tn./d
   BVS mass $= 378$ tn./d $\times$ 1000 kg/tn. $= 378 \times 10^3$ kg/d
4. Compute the amount of primary sludge required for co-digestion of the above BOF/MSW
   Assume that the TS of the primary sludge is 7% and that co-digestion occurs at 28% TS. Compute the amount of sludge needed considering the water already present in the biodegradable matter.
   Sludge required $= 1170$ tn. $= 1.17 \times 10^6$ kg/d

5. Compute the BVS mass in the primary sludge
   Assume that the VS of the primary sludge is about 70% and the biodegradable fraction of VS is about 60% of VS.
   BVS mass of primary sludge $= 1.17 \times 10^6$ lb/d $\times 0.07 \times 0.7 \times 0.6 = 34 \times 10^3$ kg/d
6. Compute the total BVS mass produced from the MSW and primary sludge
   Total BVS mass $= 378 \times 10^3$ kg/d $+ 34 \times 10^3$ kg/d $= 412 \times 10^3$ kg/d
7. Compute the biogas production rate
   Assume biogas production of about 0.86 m^3/kg BVS/d
   Total gas production rate $= (412 \times 10^3$ kg BVS/d$) \times (0.86$ m^3/kg BVS$) = 354.32 \times 10^3$ m^3/d
8. Compute the energy value of the biogas volume produced
   Assume that the thermal energy value of biogas is about 16.23 MJ/m^3
   Thermal energy $= (354.32 \times 10^3$ m^3/d$) \times (16.23$ MJ/$m^3) = 5.75 \times 10^6$ MJ/d
   Thermal energy $= (5.75 \times 10^6$ MJ/d$) \times 365$ d/year $= 2.098 \times 10^9$ MJ/yr
9. Compute the energy value relative to petroleum
   Assuming thermal energy value of one barrel of oil is about 6.218×10^6 MJ
   Energy equivalent in barrels of oil $= (2.098 \times 10^9$ MJ/yr$)/(6.218 \times 10^6$ MJ/barrel$) = 337$ barrels of oil/yr

25.1.7.7.5 Volume Reduction—Example Calculation

Computation of volume reduction for BOF/MSW and WWTPS compared to a well compacted landfill

Case 1: Sludge cake fills the interstices of the compacted MSW in the landfill

1. Assumptions
   a. Input feedstock ratio (wet): 60% sludge to 40% BOF/MSW by weight
   b. Density of compacted MSW $= 540$ kg/m^3
   c. Sludge TS $= 5\%$
2. Compute the amount of sludge required for the anaerobic composting process
   For every unit volume of BOF/MSW (540 kg of MSW) added:
   $540 \times (60/40) = 810$ kg of sludge at 5% solids is required.
3. Compute the corresponding mass of sludge dewatered to 51% solids
   Dewatering the sludge to 51% solids would reduce the sludge weight to:
   810 kg $\times (51/5) \times 0.01 = 82.6$ kg dewatered cake at 51% solids
4. Compute the combined weight of the MSW and sludge solids
   Combined weight of MSW and sludge cake $= 540 + 82.6$ kg $= 622.6$ kg
5. Compute the density of the combined MSW and sludge
   Assuming no change in MSW volume (1 m^3), combined density $= 622.6$ kg/m^3

Case 2: Sludge cake remains unmixed from compacted MSW in landfill

1. Assumptions
   a. Input feedstock ratio (wet): 60% sludge to 40% BOF/MSW
   b. Density of compacted MSW $= 540$ kg/m^3
   c. Sludge TS $= 5\%$
   d. Density of sludge cake at 51% solids $= 1240$ kg/m^3
2. Compute the amount of sludge required for the anaerobic composting process
   For every unit volume of BOF/MSW (540 kg of MSW) added:
   $540 \times (60/40) = 810$ kg of sludge at 5% solids is required.
3. Compute the corresponding mass of sludge dewatered to 51% solids
   Dewatering the sludge to 51% solids would reduce the sludge weight to:
   810 kg $\times (51/5) \times 0.01 = 82.6$ kg dewatered cake at 51% solids

4. Compute the combined weight of the MSW and sludge solids
   Combined weight of MSW and sludge cake = 540 + 82.6 kg = 622.6 kg
5. Compute the combined volume of the MSW and sludge
   a. Volume of sludge = 82.62 kg/1240 kg/m^3 = 0.07 m^3
   b. Volume of MSW = 1 m^3
   c. Combined volume = 0.07 m^3 + 1.0 m^3 = 1.07 m^3
6. Compute the combined density of the MSW and sludge (unmixed)
   Combined density = 622.6 kg/1.07 m^3 = 583 kg/m^3

25.1.8 Utilization of By-Products from In-Vessel Anaerobic Digestion Process

The principal by-product of an anaerobic composting process is biogas and a stable digestate material with a low biodegradability and high lignin content. The digestate material can be processed further to produce a high-quality humus material for marketing. The characteristics of biogas and the humus material are presented in this section.

25.1.8.1 Characteristics of Biogas

The gas produced during anaerobic digestion of biodegradable organic material in a healthy fermentation system, called biogas, consists mainly of a mixture of methane (CH_4) and carbon dioxide (CO_2) with small amounts of other gases, including hydrogen sulfide (H_2S), hydrogen (H_2), nitrogen (N_2), and low-molecular weight hydrocarbons. Typically, digester gas has 50%–75% methane and 25%–50% carbon dioxide; the remaining gases are present in very small quantities. The composition of biogas, as obtained from various sources, is reported in Table 25.14. As reported in Table 25.14, a large variation exists in the composition of biogas, primarily due to differences in feedstocks and operating conditions.

Because biogas normally consists of a mixture of gases, biogas characteristics must be evaluated for each individual case. However, in many cases, the physical characteristics of the three main gas constituents, namely methane, carbon dioxide, and hydrogen sulfide, can be used to characterize biogas. Some physical and chemical characteristics of the principal gases found in biogas are presented in Table 25.15.

As a comparison, the weight of methane is roughly half that of air at 20°C (weight ratio = 1 m^3 of methane/1 m^3 of air = 0.716 kg/1.293 kg = 0.554).

Methane gas is not very soluble in water. Only three units of methane (by volume) can be dissolved in 100 units of water at 20°C and 1 atmosphere pressure. Methane is a very stable hydrocarbon compound and upon complete combustion it produces a blue flame and a large amount of heat. The complete combustion of 1 m^3 of methane can release 38 MJ or about 9500 kcal (1 kcal of heat will raise the temperature of 1 kg of water by 1°C). In comparison, a complete combustion of biogas yields a caloric value of about 20–26 MJ/m^3 (depending on the methane content), which represents a low fuel value compared with methane gas alone. In addition, biogas requires a pressure of about 34,450 kPa

TABLE 25.14 A Typical Composition of Biogas Produced from BOF/MSW

	Percent by Volume	
Constituent	Range	Typical[a]
Methane, CH_4	50–75	53.0
Carbon dioxide, CO_2	50–25	45.0
Hydrogen sulfide, H_2S	0.01–1.5	0.02
Hydrogen, H_2	Trace-3.5[b]	1.7
Nitrogen, N_2	Trace-8[b]	Trace
Other hydrocarbon	Trace-0.05	Trace

[a] Typical biogas composition from the biodegradable organic fraction of MSW.

[b] The hydrogen and nitrogen gases reported in this table are more commonly found in landfill gases.

TABLE 25.15 Physical Characteristics of Biogas

		Average Value		
Characteristics	Unit	CO_2	CH_4	H_2S
Molecular weight	G	44.1	16.04	34.08
Vapor pressure at 21°C	kP	5719.0		1736.3
Specific volume at 21°C, 101 kP	M^3/kg	0.456	1.746	0.701
Boiling point at 101 kP	°C	−164.0	−161.61	−59.6
Freezing point at 101 kP	°C	−78.0	−182.5	−82.9
Specific gravity at 15°C (air = 1)		1.53	0.555	1.189
Density at 0 °C	kg/m^3	1.85	0.719	1.539
Critical temperature	°C	31.0	82.1	100.4
Critical pressure	kP	7386.0	4640.68	9007.0
Critical density	kg/m^3	0.468	0.162	0.349
Latent heat of vaporization at bp	kJ/kg	982.72	520.24	548.29
latent heat of fusion at mp	kJ/kg	189.0	58.74	69.78
Specific heat, Cp at 21°C, 101 kP	kJ/kg°C	0.83	2.206	1.06
Specific heat, Cv at 21°C, 101 kP	kJ/kg°C	0.64	1.688	0.803
Specific heat ratio, Cp/Cv		1.303	1.307	1.32
Thermal conductivity	W/m K	0.8323		0.0131
Flammable limits in air	% by volume		5.3–14	4.3–45
Solubility in water	kg/m^3	4.0	24.0	3.4
Viscosity	mPa s	0.0148	0.012	0.0116
Net heat of combustion at 25°C	MJ/m^3		36.71	
Gross heat of combustion at 25°C	MJ/m^3		37.97	
Ignition temperature	°C		650.0	
Octane rating			130.0	
Combustion equation			$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$H_2S + 2O_2 \rightarrow SO_3 + H_2O$[a]

[a] Reaction is temperature dependent and the final product will be sulfuric acid ($SO_3 + H_2O \rightarrow H_2SO_4$).

(5,000 lb/in.^{2}) to liquefy it for storage. Therefore, biogas requires a larger storage volume for a given amount of energy than other fossil fuels.

25.1.8.2 Utilization of Biogas

To understand the potential use of biogas, it is important to gain a perspective on its energy potential by comparing it with more familiar uses of energy. The following are some examples of the use of 1 m^3 of biogas, at 60%–70% methane content, for common energy-consuming purposes (see Table 25.16):[39]

The potential commercial uses of biogas as a source of energy are summarized in Table 25.17. Some applications listed in Table 25.17 are presently practiced and others are in the process of research and development.

TABLE 25.16 Equivalent Uses of Biogas

Use	Equivalent Use
Cooking	Can cook three meals for a family of five to six
Lighting	Illumination equaling that of 60–100 W bulb for 6 h
Petroleum	Equivalent to 0.76 kg of petroleum
Car fuel	Can drive a 3 tn. truck 2.8 km
Motor power	Can run a 1 horse-power motor for 2 h
Electricity	Can generate 1.25 kW electricity

Source: Adapted from Barnett, A., Pyle, L., Subramanian, K. S., *Biogas Technology in the Third World: A Multidiciplinary Review*, International Development Research Center, Ottawa, Canada, 1978.

TABLE 25.17 Uses for Biogas Produced from the Biodegradation of the Organic Fraction of MSW

Applications	Comment
Fuel in an IC engine	The most common application of biogas, usually used to generate electricity. Modified engines available from Caterpillar, Cooper-Superior, and Waukesha. Modifications include corrosion resistance and proprietary designing. Specialized lubricating oils are necessary and must be changed more often. Power ratings are usually 5%–15% below natural gas ratings
Fuel in a gas turbine	Common application of biogas, used to produce electricity Modifications similar to those for IC engines are necessary. Biogas turbines are made by the Solar turbine division of Caterpillar. Power rating is 10–15% lower than for natural gas. Turbines must be checked often for corrosion or deposition. Water vapor should be removed from biogas before use
Boiler fuel	In moderate use, presently, requires little modification to present equipment. A mixture of biogas and natural gas may be used. Boilers appear to be less sensitive to gas contaminants than IC engines or gas turbines
Pipeline quality gas	Less common use. CO_2 and all contaminant gases, including water vapor, must be removed before gas will be accepted into a pipeline. Usually, not economical unless a large amount of gas is produced and a long-term contract for the sale is available
Fuel in a steam turbine	Presently in limited use. A large amount of gas is necessary before the system will be economical for the production of electricity. However, modifications are small
Fuel for space heating	Presently in limited use. Only minor modifications necessary to convert equipment which uses natural gas. Economical even on a small scale. Hampered only by unavailability of gas. Pipelines are not presently economical, so only used at production sites
Fuel for industrial heating	Presently in limited use. Can be used for lumber drying, kiln operations, and cement manufacturing. May be used in place of or with natural gas, using natural gas equipment
Fuel for fuel cell	Technology under development. These open fuel batteries can be designed to use biogas, or biogas can be converted to hydrogen in a catalytic pretreatment unit
Compressed vehicle fuel	Technology under development. Gas must be purified to near pipeline quality
Convert to methanol	Technology under development. Presently too costly
Synfuel or chemical feedstock	Technology under development. Liquid fuels and acetic acid production is being investigated

25.1.8.3 Characteristics of Digested Biosolids (Humus Material)

The physical, chemical, and biological characteristics of the humus produced from an anaerobic composting using the sorted biodegradable organic fraction of MSW are presented in this section. The data reported in this section were obtained from the UC Davis pilot demonstration project.[35,40]

TABLE 25.18 Physical Characteristics of Humus Produced from BOF/MSW by the Anaerobic Composting Process

Item	Unit	Value or Description
Bulk density	kg/m^3	560
Color		Dark brown
Moisture content	%	35
Odor		No offensive odor detected
Particle Size Distribution		
8 (2.362 mm)[a]	% of TM[b]	11.9
20 (0.833 mm)	% of TM	28.9
40 (0.351 mm)	% of TM	25.4
80 (0.175 mm)	% of TM	21.3
100 (0.147 mm)	% of TM	7.8
200 (0.074 mm)	% of TM	4.3
Pan	% of TM	0.4

[a] Sieve number (size, mm).

[b] TM = total mass (sample at 65% total solids).

Source: From Kayhanian, M. and Tchobanoglous, G., *Environmental Technology*, 14, 815–829, 1993.

The physical characteristics of the humus which are of interest are bulk density, color, moisture content, odor, and particle size distribution. The physical characteristics of the humus are summarized in Table 25.18. The chemical characteristics of the humus which are of interest can be determined by ultimate analysis, metal analysis, fiber analysis, nutrient analysis, energy content, and other tests. The chemical characteristics of the humus are summarized in Table 25.19. The biological characteristics of the humus which are of interest are the presence and the concentration of pathogenic bacterial, biodegradability, and phytotoxicity. The biological characteristics of the humus are summarized in Table 25.20.

25.1.8.4 Utilization of Humus Material

Representative applications for the humus produced from anaerobic digestion processes are summarized in Table 25.21. The most effective use of the humus material is as a soil amendment. Alternatively, because the humus is combustible, it appears that it can be fired directly in a boiler, when mixed with other fuels, or palletized for use as a fuel source. The application of the humus as a fuel source has been further studied and readers are referred to Jenkins et al.[41]

It is important to note that, depending on the final use, further aerobic composting of the digestate may be necessary to produce humus with no phytotoxic affect to be used as a soil amendment. For other applications specified in Table 25.21, no further stabilization may be needed.

25.1.9 Commercial-Scale In-Vessel Anaerobic Digestion Technologies

In the U.S., initial efforts to commercialize anaerobic digestion technology for converting biomass into energy and other products have been conducted primarily by livestock enterprises. The barrier to commercialization of anaerobic technology in the U.S. has been described by Lusk.[21] In addition, the commercial firms interested in the technology, the economics of the process, the statutes which apply, and the future prospects for application in the U.S. are identified and discussed. In general, the biggest barriers up to now have been financial rather than technical in nature. With rising energy costs and examples of successful anaerobic digester operation, more interest has been generated recently in these systems. Most large-scale anaerobic digestion applications for methane recovery in the U.S. are related to animal waste and wastewater treatment.[20,21] For instance, two large-scale farm digesters have been in operation in California since 1980.[21]

TABLE 25.19 Chemical Characteristics of the Humus Produced from BOF/MSW by the Anaerobic Composting Process

Chemical Analyses	Unit[a]	Range	Typical
Ultimate Analysis			
Carbon, C	%	30–35	32.4
Hydrogen, H	%	3.5–4	3.8
Chlorine, Cl	%	0.05–0.4	0.30
Nitrogen, N	%	1–2	1.9
Oxygen, O	%	30–35	31.4
Residue	%	25–35	30
Sulfur, S	%	0.1–0.4	0.25
Metal Analysis			
Aluminum, Al	mg/kg	30–194	54
Argon, Ar	mg/kg	<1–2	0.13
Arsenic, As	mg/kg	<1–3	1.04
Boron, B	mg/kg	12–64	18
Cadmium, Cd	mg/kg	<1–5	1.55
Calcium, Ca	%	0.8–1.7	1.08
Chromium, Cr	mg/kg	5–35	13
Cobalt, Co	mg/kg	<1–1	0.5
Copper, Cu	mg/kg	18–248	30
Iron, Fe	mg/kg	100–710	170
Lead, Pb	mg/kg	5–43	7
Magnesium, Mg	%	0.3–0.5	0.34
Manganese, Mn	mg/kg	120–175	133
Molybdenum, Mo	mg/kg	1–20	6
Nickel, Ni	mg/kg	18–186	28
Selenium, Se	mg/kg	<1	<1
Silicon, Si	mg/kg	0.1–4	0.21
Sodium, Na	%	0.1–0.3	0.3
Tungsten, W	mg/kg	<1–10	0.3
Zinc, Zn	mg/kg	98–376	176
Fiber Analysis			
Cellulose	%		35.3
Hemicellulose	%		3.9
Lipid	%		1.45
Protein	%		11.9
Lignin	%		26.5
Nutrient Analysis			
Nitrogen, N	%	1–2	1.9
Phosphorus, P	%	0.1–0.5	0.23
Phosphate, PO_4-P	mg/kg	50–200	170
Potassium, K	%	0.3–1	0.73
Sulfate, SO_4-S	mg/kg	300–800	547
Energy Content, HHV	MJ/kg	13–15	14.8
Others			
Cation exchange capacity, CEC meq/100 g dry		20–100	30
Electrical conductivity, EC	millimho/cm	5–15	9.4
PH		7–8.5	8.2

[a] % and mg/kg are based on dry mass.

Source: From Kayhanian, M. and Tchobanoglous, G., *Environmental Technology*, 14, 815–829, 1993.

A number of studies have been performed in the U.S. to utilize the anaerobic digestion process for methane gas recovery from solid waste materials.[13,23,31,35,42–46] Unfortunately, none of these projects have commercialized or implemented at full scale. Western Europe has been a leader in developing new solutions for managing MSW.[47] Germany and France, for example, have large-scale composting

TABLE 25.20 Biological Characteristics of the Humus Produced from the BOF/MSW by the Anaerobic Composting Process

Item	Unit	Value
Bacterial Concentration		
Total coliform	MPN/100 ml	Not detected[a]
Fecal coliform	MPN/100 ml	Not detected
Streptococcus and Enterococcus	MPN/100 ml	Not detected
Residual Biodegradability		
Biodegradable fraction	%VS	8.8[b]
Phytotoxicity		
Seed germinated with 100% leachate concentration	%	0[c]
Seed germinated with 20% leachate concentration	%	78
Seed germinated with 15% leachate concentration	%	95

[a] Detection limit is 0–6 organisms/10 ml at 95% confidence level.

[b] Biodegradable fraction (BF) is computed based on the lignin content (LC) presented in Table 25.19, using Equation 25.1: $BF = 0.83 - (0.028) \times LC$.

[c] Percent seed germinated is computed based on the ratio of seed germinated at each dilution, compared to the control.

Source: From Kayhanian, M. and Tchobanoglous, G., *Environmental Technology*, 14, 815–829, 1993.

plants in operation, and many of the recent innovations in the waste-to-energy industry have come from European countries. In 2005, De Baere, reviewed the state-of-the-art application of anaerobic digestion of MSW in Europe. Presently, there are 124 full-scale anaerobic digestion plants have been constructed in Europe by 27 suppliers.[48] Only three have constructed more than 15 plants based on the same concept. The suppliers include Dranco, Valorga, and Kompgas.

Two commercialized systems, the Dranco and Valorga, have been in operation at full scale in Europe since the late 1980s. The Kompgas process has been applied since 1990. All three of these European technologies employ high-solids digestion operated at TS concentrations of 20%–35%, thus achieving higher rates of gas production than have been reported from the conventional, low-solids anaerobic digestion of wastewater sludge or other natural organic materials. These three anaerobic digestion systems are the only commercial operations in the world that have performance data and a track

TABLE 25.21 Uses for Humus Material Produced from Anaerobic Digestate

Applications	Remarks
Use as soil amendment	The humus must be odorless, low in heavy metals, and free of pathogens. In addition, the amount of humus applied to the topsoil may be limited by the phytotoxic characteristics of the humus
Use as turf for sod production	Similar restrictions apply as specified for use of humus as a soil amendment
Use as topsoil for erosion control	If humus is to be used for the control of agricultural soil erosion, it must be of similar quality to that specified for soil amendments. For other erosion control applications, specifications may be less restrictive
Use as topsoil for landfills cover	Moisture content should be greater than about 35% to avoid wind erosion
Use as marsh restoration	Humus can be used to build up the organic material required for the growth of marsh plants in marsh restoration projects. A higher degree of humus stabilization may be required for this application
Use as absorbent agent for control and Humus may be used as an absorbent to limit	
Movement of hazardous wastes	Movement of liquid hazardous wastes
Use as fuel or fuel blend in power plants	Major characteristics of concern include: moisture content, foreign matter, heating value, and environmental impact on air quality

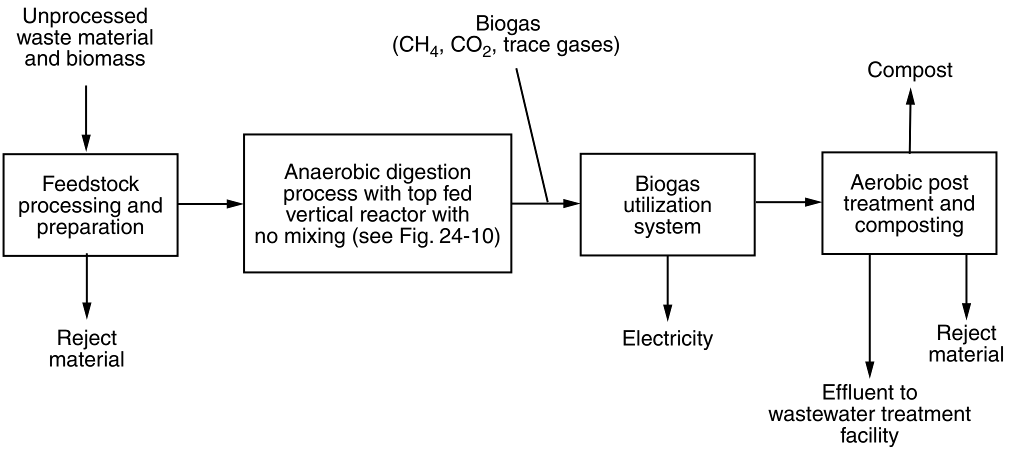

FIGURE 25.9 Schematic flow diagram of the DRANCO process.

record for over 15 years. The operational characteristics of these three systems are reviewed briefly below.

25.1.9.1 Dranco System

The Dranco (Dry ANaerobic COmposting) process (see Figure 25.9) was developed in Ghent, Belgium for the high-solids anaerobic digestion of refuse derived fuel (RDF). The RDF is prepared by completely sorting incoming urban solid waste. The Dranco system[49–51] is capable of removing most metals, glass, plastic, stone, recoverable paper, and other non-biodegradable items.

The anaerobic treatment takes place in a vertical fermenter (see Figure 25.10) for a period of 12–18 days, followed by a post-fermenter for a retention time of 2–3 days. The overall digestion time is, therefore, 14–21 days. The feed is mixed with recycled digester effluent and supernatant, and then pumped into the top of the reactor at a solids concentration of 355%–40%. Solids move downward in the digester in a plug-flow manner, without mechanical mixing. The digester operates under mesophilic (35°C) conditions with a VS reduction of about 55%. Presently, nine full-scale plants are operational in Europe and the capacity of each plant varies from 10,000 to 50,000 metric ton of MSW per year.

The solids are dewatered from about 30% to around 70% solids using a filter press and are dried further and marketed as compost, while the supernatant is used to dilute incoming feed. Additional information on the Dranco system can be obtained from the following web address: http://www.ows.be.

25.1.9.2 Valorga System

Valorga, a French company, was the first to use anaerobic technology for the treatment of MSW.[52,53] The complete Valorga system (see Figure 25.11) can be divided into five subunits: (1) preparation, (2) methanization, (3) biogas treatment, (4) combustion of combustible refuse, and (5) refining. The Valorga digester is distinguished by its unique design and is operated at a solids concentration of 35% under mesophilic (35°C) conditions with a retention time of 15 days. A typical Valorga reactor capacity is 500 m^3, and it can treat from 20 to 28 tn. of RDF per day. The VS removal rate is around 50% and the average gas production is about 140 m^3 biogas per ton of feed.

Two unique features of the Valorga process are: (1) the loading and (2) mixing mechanisms (see Figure 25.12). A piston pump is used to load feedstock into the system, supplying the digestion system with feed on a continuous basis. A control isolation valve system injects sufficient pressure to transfer the

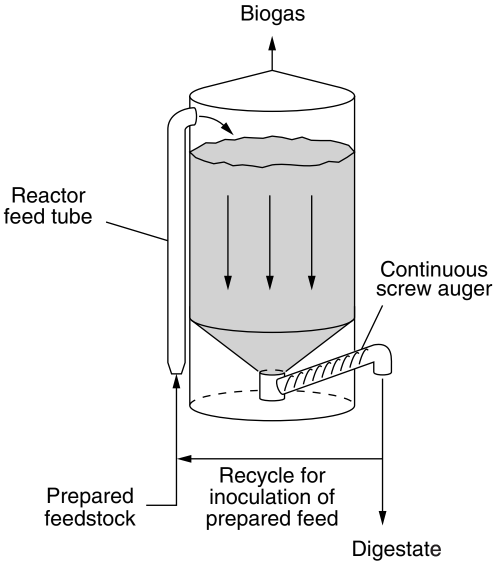

FIGURE 25.10 Schematic of the DRANCO anaerobic reactor. (Adapted from http://www.ows.be).

feedstock into the digester; at the same time, a similar quantity of digestate is extracted from the outlet. Mixing takes place through the programmed injection of pressurized biogas into a different section of the system.

Valorga has the most developed MSW anaerobic digestion technology in the world and over 15 full-scale plants are operational in various countries in Europe.[48] One large-scale Valorga system has been in operation in France since 1987. Three Valorga systems with annual capacity of over 200,000 metric ton became operational in various cities in Spain since 1999. Additional information on the Valorga system can be obtained from the following web address: http://www.valorgainternational.fr/index_en.php.

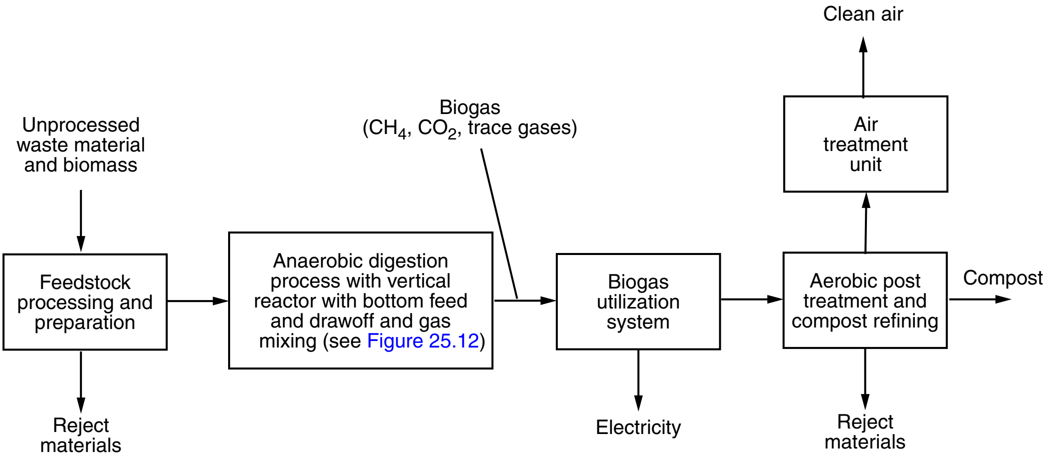

FIGURE 25.11 Schematic flow diagram of the VALORGA process.

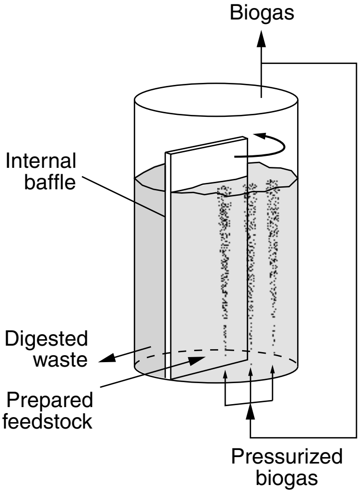

FIGURE 25.12 Schematic of the Valorga anaerobic reactor. (Adapted from http://www.valorgainternational.fr/index_en.php).

25.1.9.3 Kompogas System

Kompogas technology was developed in Switzerland and is generally composed of four major components (see Figure 25.13): (1) feedstock preparation, (2) digestion process, (3) biogas processing and utilization, and (4) digestate processing and compost production. Most Kompogas plants operate by using the source-separated mixture of easily biodegradable kitchen, food, and industrial wastes combined with wastes from gardens. To prepare the digester feed, a portion of the digestion slurry is mixed with the incoming biodegradable wastes.

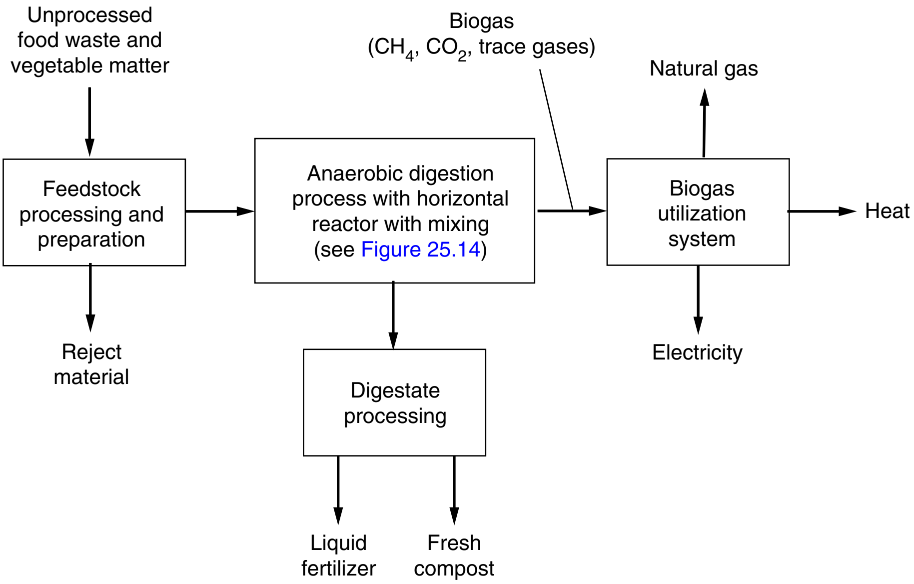

FIGURE 25.13 Schematic flow diagram of the Kompogas process.

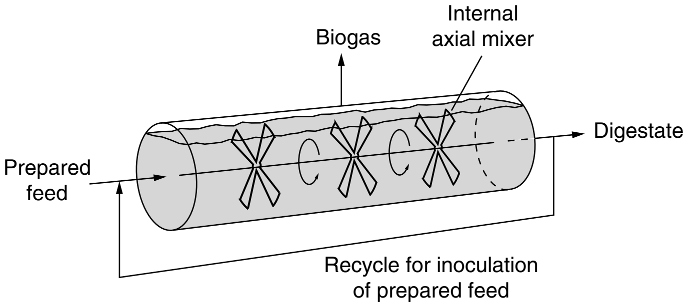

FIGURE 25.14 Schematic of the Kompogas anaerobic reactor. (Adapted from http://www.kompogas.com).

The Kompogas digester consists of a horizontal, cylindrical plug-flow reactor that operates under thermophilic temperature and solid content of about 20%. The reactor content is gently mixed along the longitudinal axis. A simplified diagram of Kompogas digester is shown in Figure 25.14. The horizontal design, with an agitation only right-angled to the flow direction, guarantees a good plug-flow behavior. The horizontal reactor design seems to be advantageous regarding clogging and sedimentation compared with vertical reactor designs.[54] With a few exceptions, nearly all Kompogas digesters are made out of steel.

At present, 22 large-scale Kompogas plants are in operation in Europe and elsewhere. Nine of these plants are located in Switzerland and the remaining thirteen plants are located in Japan, Germany, Denmark, Spain, and Astoria. Additional information on the Kompogas system can be obtained from the following web address: http://www.kompogas.com.

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25.2 Power Generation

Robert C. Brown

25.2.1 Introduction

Although biomass encompasses many kinds of organic matter, fibrous plant material can be characterized as solid, carbonaceous fuel of high volatile content and heating value of about 18 MJ/kg.[1] Either direct combustion or thermal gasification can be used to transform this chemical energy into electric power. Direct combustion releases heat that can be used in Stirling engines or Rankine steam power cycles. Thermal gasification yields flammable gases suitable for firing in internal combustion engines, gas turbines, or fuel cells.

25.2.2 Direct Combustion

Combustion is the rapid oxidation of fuel to obtain energy in the form of heat. Since biomass fuels are primarily composed of carbon, hydrogen, and oxygen, the main oxidation products are carbon dioxide and water although fuel-bound nitrogen can be a source of significant nitrogen oxide emissions. Depending on the heating value and moisture content of the fuel, the amount of air used to burn the fuel, and the construction of the furnace, flame temperatures can exceed 1650°C.

Solid fuel combustion consists of four steps, which are illustrated in Figure 25.15: heating and drying, pyrolysis, flaming combustion, and char combustion.[2] Heating and drying of the fuel particle is normally not accompanied by chemical reaction. Water is driven from the fuel particle as the thermal front advances into the interior of the particle. As long as water remains, the temperature of the particle does not raise high enough to initiate pyrolysis, which is the second step in solid fuel combustion.

Pyrolysis is a complicated series of thermally driven chemical reactions that decompose organic compounds in the fuel. Pyrolysis proceeds at relatively low temperatures, which depend on the type of plant material. Hemicellulose begins to pyrolyze at temperatures between 150 and 300°C, cellulose pyrolyzes at 275°C–350°C and lignin pyrolysis is initiated between 250 and 500°C.[3]

The resulting decomposition yields a large variety of volatile organic and inorganic compounds; the types and amounts dependent on the fuel and the heating rate of the fuel. Pyrolysis products include

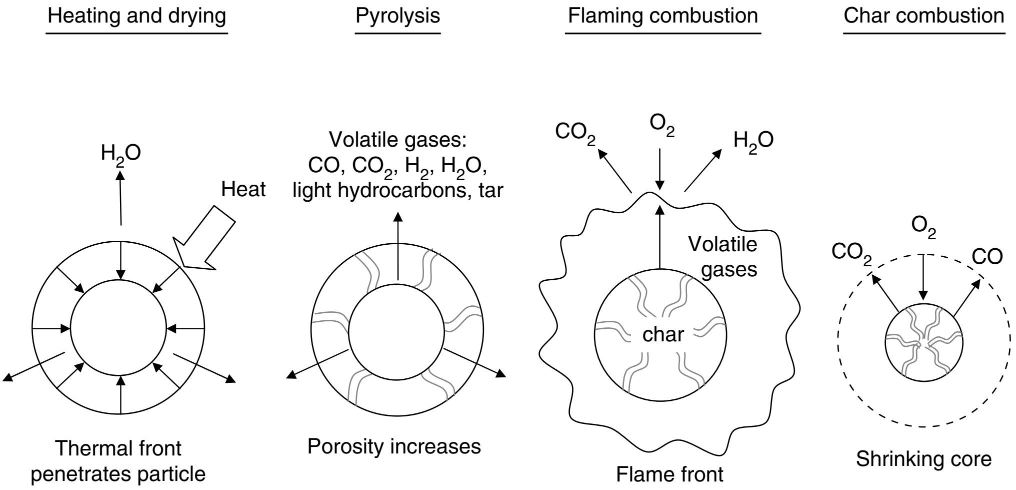

FIGURE 25.15 Processes of solid fuel combustion. (From Brown, R. C., *Biorenewable Resources: Engineering New Products from Agriculture*, Iowa State Press, Ames, IA, 2003.)

carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and high molecular weight compounds that condense to a tarry liquid if cooled before they are able to burn. Fine droplets of these condensable compounds represent much of the smoke associated with smoldering fires. Pyrolysis follows the thermal front through the particle, releasing volatile compounds and leaving behind pores that penetrate to the surface of the particle.

Pyrolysis is very rapid compared with the overall burning process and may be as short as a second for small particles of fuel but can extend to many minutes in wood logs. Although the net result of combustion is oxidation of fuel molecules and the release of heat, neither of these processes occurs to a significant extent during pyrolysis. Indeed, if pyrolysis is to proceed at all, heat must be added to the fuel. Oxygen is excluded from the pyrolysis zone by the large gaseous outflux of pyrolysis products from the surface of the fuel particle. Only after pyrolysis gases escape the particle and diffuse into the surrounding air, they are able to burn. There remains upon completion of pyrolysis a porous carbonaceous residue known as char.

Both the volatile gases and the char resulting from pyrolysis can be oxidized if sufficient oxygen is available to them. Oxidation of the volatile gases above the solid fuel results in flaming combustion. The ultimate products of volatile combustion are CO_2 and H_2O although a variety of intermediate chemical compounds can exist in the flame, including CO, condensable organic compounds, and long chains of carbon known as soot. Indeed, hot, glowing soot is responsible for the familiar orange color of wood fires.

Combustion intermediates will be consumed in the flame if sufficient temperature, turbulence, and time are allowed. High combustion temperature assures that chemical reactions will proceed at high rates. Turbulent or vigorous mixing of air with the fuel makes certain that every fuel molecule comes into contact with oxygen molecules. Long residence times for fuel in a combustor allow the fuel to be completely consumed. In the absence of good combustion conditions, a variety of noxious organic compounds can survive the combustion process including CO, soot, polycyclic aromatic hydrocarbons (PAH), and the particularly toxic families of chlorinated hydrocarbons known as furans and dioxins. In some cases, a poorly operated combustor can produce pollutants from relatively benign fuel molecules.

The next step in combustion of solid fuels is solid–gas reactions of char, also known as glowing combustion, familiar as red-hot embers in a fire. Char is primarily carbon with a small amount of mineral matter interspersed. Char oxidation is controlled by mass transfer of oxygen to the char surface rather than by chemical kinetics, which is very fast at the elevated temperatures of combustion. Depending on the porosity and reactivity of the char and the combustion temperature, oxygen may react with char at the surface of the particle or it may penetrate into the pores before oxidizing char inside the particle. The former situation results in a steadily shrinking core of char whereas the latter situation produces a constant diameter particle of increasing porosity. Both CO and CO_2 can form at or near the surface of burning char:[2]

$$\mathrm{C} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO} \tag{25.6}$$

$$\mathrm{CO} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO_2} \tag{25.7}$$

These gases escape the immediate vicinity of the char particle where CO is oxidized to CO_2 if sufficient oxygen and temperature are available; otherwise, it appears in the flue gas as a pollutant.

25.2.3 Combustion Equipment

A combustor is a device that converts the chemical energy of fuels into high temperature exhaust gases. Heat from the high temperature gases can be employed in a variety of applications, including space heating, drying, and power generation. However, with the exception of kilns used by the cement industry, most solid fuel combustors today are designed to produce either low-pressure steam for process heat or high-pressure steam for power generation. Combustors integrated with steam-raising equipment are called boilers. In some boiler designs, distinct sections exist for combustion, high temperature heat transfer, and moderate temperature heat transfer: these are called the furnace, radiative, and convective sections of the boiler, respectively. In other designs, no clear separation between the processes of combustion and heat transfer exists.

Solid fuel combustors, illustrated in Figure 25.16, can generally be categorized as grate-fired systems, suspension burners, or fluidized beds.[4] Grate-fired systems were the first burner systems to be developed, evolving during the late nineteenth and early twentieth centuries into a variety of automated systems. The most common system is the spreader-stoker, consisting of a fuel feeder that mechanically or pneumatically flings fuel onto a moving grate where the fuel burns. Much of the ash falls off the end of the moving grate although some fly ash appears in the flue gas. Grate systems rarely achieve combustion efficiencies exceeding 90%.

Suspension burners were introduced in the 1920s, as a means of efficiently burning large quantities of coal pulverized to less than fifty micron particle sizes. Suspension burners suspend the fuel as fine powder in a stream of vertically rising air. The fuel burns in a fireball and radiates heat to tubes that contain water to be converted into steam. Suspension burners, also know as pulverized coal (PC) boilers, have dominated the U.S. power industry since World War II because of their high volumetric heat release rates and their ability to achieve combustion efficiencies often exceeding 99%. However, they are not well suited to burn coarse particles of biomass fuel and they are notorious generators of nitrogen oxides. Biomass is fed from a bunker through pulverizers designed to reduce fuel particle size enough to burn in suspension. The fuel particles are suspended in the primary airflow and fed to the furnace section of the boiler through burner ports where it burns as a rising fireball. Secondary air injected into the boiler helps to complete the combustion process. Heat is absorbed by steam tubes arrayed in banks of heat exchangers (waterwall, superheaters, and economizer) before exiting through a bag house designed to capture ash released from the fuel. Steam produced in the boiler is part of a Rankine power cycle.

Fluidized bed combustors are a recent innovation in boiler design. Air injected into the bottom of the boiler suspends a bed of sand or other granular refractory material producing a turbulent mixture of air and sand. The high rates of heat and mass transfer in this environment are ideal for efficiently burning a

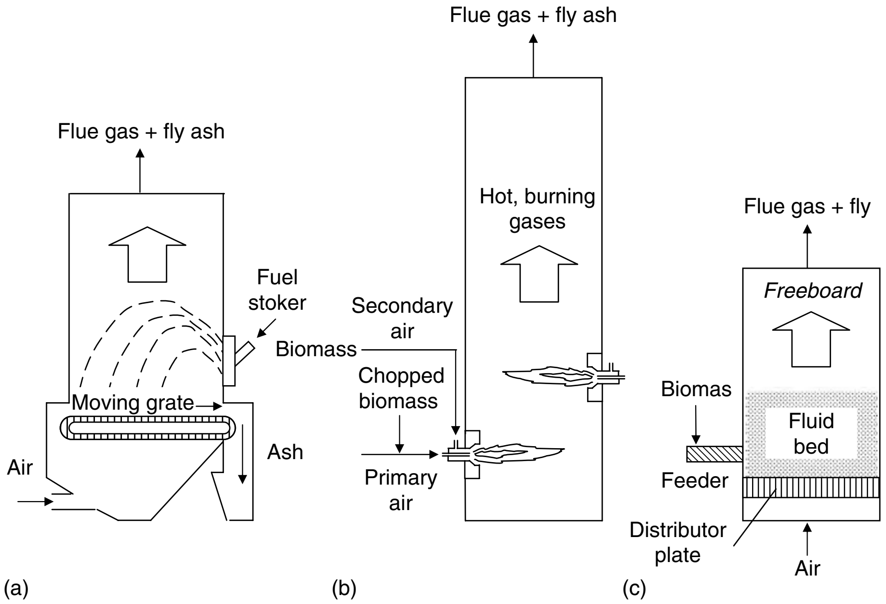

FIGURE 25.16 Common types of combustors: (a) grate-fired, (b) suspension, (c) fluidized bed. (From Brown, R. C., *Biorenewable Resources: Engineering New Products from Agriculture*, Iowa State Press, Ames, IA, 2003.)

variety of fuels. Furthermore, the large thermal mass of the sand bed allows the unit to be operated as low as 850°C, which lowers the emission of nitrogen compounds. A commercial market for fluidized bed boilers developed during the 1980s, especially for industrial applications.

Whole-tree burners have been proposed for electrical utility steam raising. The advantage of this approach is minimization of field processing and handling and the elimination of fuel chipping, which can save about 35% of the cost of harvesting and handling woody fuels.

A variety of biomass materials have proven suitable for direct combustion, including whole trees, wood chips, forestry residue, agricultural residue, pulp and paper refuse, food processing wastes, municipal solid waste, and straws and grasses. Wood and wood wastes dominate the biomass-to-power market in the U.S. and much of the rest of the world. However, a variety of agricultural wastes have been utilized through direct combustion in California, and Denmark has a number of commercial plants that burn straw.

Direct combustion has the advantage that it employs commercially well-developed technology. There are a number of vendors who supply turnkey systems and considerable operating experience and exists both in the U.S. and abroad. However, there are three prominent disadvantages with direct firing. These include penalties associated with burning high moisture fuels, agglomeration, and ash fouling due to alkali compounds in biomass, and relatively low thermodynamic efficiencies for steam power plants of the size appropriate to biomass power.

The moisture in biomass degrades boiler performance for two reasons. First, the energy required to vaporize fuel moisture can only be recovered if exhaust gases are cooled sufficiently to condense the water vapor in this gas. Although this procedure would result in very high thermal efficiencies for a boiler burning even very high moisture fuels, it is not commonly done in practice because the condensate is often corrosive to boiler tubes. Accordingly, most direct-combustion systems are penalized by moisture in the fuel. Second, high moisture fuels simply do not burn well because the process of fuel drying suppresses fuel temperatures below that required for ignition. Water contents exceeding 30% are unacceptable in most boilers for this reason. However, fluidized bed combustors, because of the enormous thermal mass associated with the hot bed material, can accept biomass with moisture content as high as 50% although even fluidized beds are penalized in thermal efficiency by the presence of this moisture. Depending on moisture content, as much as 15% of the heating value of biomass is required to dry the fuel. Obviously, field drying of biomass is desired to reduce both transportation costs and heating penalties within the boiler.

Alkali in biomass fuels presents a difficult problem for direct combustion systems. Compounds of alkali metals, such as potassium and sodium salts, are common in rapidly growing plant tissues. Annual biomass crops contain large quantities of alkali while the old-growth parts of perennial biomass contain relatively small quantities of alkali. These alkali compounds appear as oxides in the residue left after combustion of volatiles and char. Alkali vapors may combine with sulfur and silica to form low-melting point compounds.[5] These sticky compounds bind ash particles to fuel grates and heat exchanger surfaces. Boiler performance degrades as airflow and heat transfer are restricted by ash deposits. Boilers that fire straw, which contain both high silica and alkali, have experienced serious problems in slagging and fouling, as well as high temperature corrosion unless steam temperatures are kept relatively low (less than 500°C).

As an alternative to completely replace coal with biomass fuel in a boiler, mixtures of biomass and coal can be burned together in a process known as co-firing.[6] Co-firing offers several advantages for industrial boilers. Industries that generate large quantities of biomass wastes, such as lumber mills or pulp and paper companies, can use co-firing as an alternative to costly landfilling of wastes. Federal regulations also make co-firing attractive. The New Source Performance Standards, which limits particulate emissions from large coal-fired industrial boilers to 0.05 lb/MM Btu, doubles this allowance in co-fired boilers in which the capacity factor for biomass exceeds 10%. Adopting co-firing is a good option for companies that are slightly out of compliance with their coal-fired boilers. Similarly, a relatively inexpensive method for a company to reduce sulfur emissions from its boilers is to co-fire with biomass, which contains much less sulfur than coal. Co-firing capability also provides fuel flexibility and reduces ash-fouling problems associated with using only biomass as fuel.

The principal disadvantages of co-firing relate to the characteristics of biomass fuels. Because of the lower energy density and higher moisture content of biomass, the steam generating capacity of co-fired boilers is often reduced. Also, the elemental composition of fly ash from biomass is distinct from that of coal fly ash. Utilities are concerned that comingled biomass and coal ash will not meet the American Society for Testing and Materials (ASTM) definition of fly ash that is acceptable for concrete admixtures, thus eliminating an important market for this combustion by-product.

It is generally recommended that total fuel (single or mix) alkali content be limited to less than 0.17–0.34 kg/GJ (0.4–0.8 lb/MM Btu), which translates to only 5%–15% co-firing of biomass with coal. Also, furnace temperatures should be kept below 980°C to help to prevent the buildup of alkali-containing mineral combinations known as eutectics. At higher temperatures, molten eutectics bind dirt and other particulates to form slag and fouling deposits.

The best wood-fired power plants, which are typically 20–100 MW in capacity, have heat rates exceeding 12,500 Btu/kWh. In contrast, large, coal-fired power plants have heat rates of only 10,250 Btu/kWh. The relatively low thermodynamic efficiency of steam power plants at the sizes of relevance to biomass power systems may ultimately limit the use of direct combustion to convert biomass fuels to useful energy.

25.2.4 Thermal Gasification

Gasification is the high temperature (750°C–850°C) conversion of solid, carbonaceous fuels into flammable gas mixtures, sometimes known as producer gas, consisting of carbon monoxide (CO), hydrogen (H_2), methane (CH_4), nitrogen (N_2), carbon dioxide (CO_2), and smaller quantities of higher hydrocarbons. The overall process is endothermic and requires either the simultaneous burning of part of the fuel or the delivery of an external source of heat to drive the process.[7]

Gasification was placed into commercial practice as early as 1812, when coal was converted to gas for illumination (known as manufactured gas or town gas) in England. This technology was widely adopted in industrialized nations and was employed in the U.S. as late as the 1950s, when interstate pipelines made inexpensive supplies of natural gas available.[8] Some places, like China, still manufacture gas from coal.

The high volatile content of biomass (70–90 wt%) compared with coal (typically 30–40 wt%) and the high reactivity of its char make biomass an ideal gasification fuel. However, issues of cost and convenience of biomass gasification has limited its applications to special situations and niche markets. For example, in response to petroleum shortages during World War II, over one million small-scale wood gasifiers were built to supply low enthalpy gas for automobiles and steam boilers.[7] These were abandoned soon after the war.

Not only can producer gas be used for generation of heat and power, it can serve as feedstock for production of liquid fuels and chemicals. Because of this flexibility of application, gasification has been proposed as the basis for "energy refineries" that would provide a variety of energy and chemical products, including electricity and transportation fuels.

25.2.4.1 Fundamentals of Gasification

Figure 25.17 illustrates the several steps of gasification: heating and drying, pyrolysis, solid–gas reactions that consume char, and gas-phase reactions that adjust the final chemical composition of the producer gas.[9] Drying and pyrolysis are similar to the corresponding processes for direct combustion described in the previous section. Pyrolysis begins between 300 and 400°C and produces the intermediate products of char, gases (mainly CO, CO_2, H_2, and light hydrocarbons), and condensable vapor (including water, methanol, acetic acid, acetone, and heavy hydrocarbons). The distribution of these products depends on chemical composition of the fuel and the heating rate, and temperature achieved in the reactor. However, the total pyrolysis yield of pyrolysis products and the amount of char residue can be roughly estimated from the proximate analysis of the fuel. The fuel's volatile matter roughly corresponds to the pyrolysis yield, while the combination of fixed carbon and ash content can be used to estimate the char yield.

Heating and drying are endothermic processes, requiring a source of heat to drive them. This heat can be supplied by an external source in a process called indirectly heated gasification. More typically, a small amount of air or oxygen (typically not more than 25% of the stoichiometric requirement for complete combustion of the fuel) is admitted for the purpose of partial oxidation, which releases sufficient heat for drying and pyrolysis as well as for the subsequent endothermic chemical reactions described below.

The third step of gasification is solid–gas reactions. These reactions convert solid carbon into gaseous CO, H_2, and CH_4:[10]

$$\text{Carbon–oxygen reaction}: \quad C + \frac{1}{2}O_2 \leftrightarrow CO \quad \Delta H_R = -110.5\ \text{MJ/kmol} \tag{25.8}$$

$$\text{Boudouard reaction}: \quad C + CO_2 \leftrightarrow 2CO \quad \Delta H_R = 172.4\ \text{MJ/kmol} \tag{25.9}$$

$$\text{Carbon–water reaction}: \quad C + H_2O \leftrightarrow H_2 + CO \quad \Delta H_R = 131.3\ \text{MJ/kmol} \tag{25.10}$$

$$\text{Hydrogenation reaction}: \quad C + 2H_2 \leftrightarrow CH_4 \quad \Delta H_R = -74.8\ \text{MJ/kmol} \tag{25.11}$$

The first of these, known as the carbon–oxygen reaction, is strongly exothermic and is important in supplying the energy requirements for drying, pyrolysis, and endothermic solid–gas reactions. The hydrogenation reaction also contributes to the energy requirements of the gasifier, although significantly more char reacts with oxygen than hydrogen in the typical air-blown gasifier.

The fourth step of gasification is gas-phase reactions, which determine the final mix of gaseous products:[10]

$$\text{Water–gas shift reaction}: \quad CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta H_R = -41.1\ \text{MJ/kmol} \tag{25.12}$$

$$\text{Methanation}: \quad CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H_R = -206.1\ \text{MJ/kmol} \tag{25.13}$$

The final gas composition is strongly dependent on the amount of oxygen and steam admitted to the reactor as well as the time and temperature of reaction. For sufficiently long reaction times, chemical equilibrium is attained and the products are essentially limited to the light gases CO, CO_2, H_2, and CH_4 (and nitrogen if air was used as a source of oxygen). Analysis of the chemical thermodynamics of these six gasification reactions reveals that low temperatures and high pressures favor the formation of CH_4, whereas high temperatures and low pressures favor the formation of H_2 and CO.

Often gasifier temperatures and reaction times are not sufficient to attain chemical equilibrium and the producer gas contains various amounts of light hydrocarbons such as C_2H_2 and C_2H_4 as well as up to 10 wt% heavy hydrocarbons that condense to a black, viscous liquid known as "tar."[12] This latter product is undesirable as it can block valves and filters and interferes with downstream conversion processes. Steam injection and addition of catalysts to the reactor are sometimes used to shift products toward lower-molecular weight compounds.

25.2.4.2 Gasification Equipment

Gasifiers are generally classified according to the method of contacting fuel and gas. The four classes of gasifiers are updraft (countercurrent), downdraft (concurrent), fluidized bed, and entrained flow.[12] These are illustrated in Figure 25.18 while their performance characteristics are summarized in Table 25.22.

Updraft gasifiers, illustrated in Figure 25.18a, are the simplest as well as the first type of gasifier developed. They were a natural evolution from charcoal kilns, which yield smoky yet flammable gas as a waste product, and blast furnaces, which generate product gas that reduces ore to metallic iron. Updraft gasifiers are little more than grate furnaces with chipped fuel admitted from above and insufficient air for complete combustion entering from below. Above the grate, where air first contacts the fuel, combustion

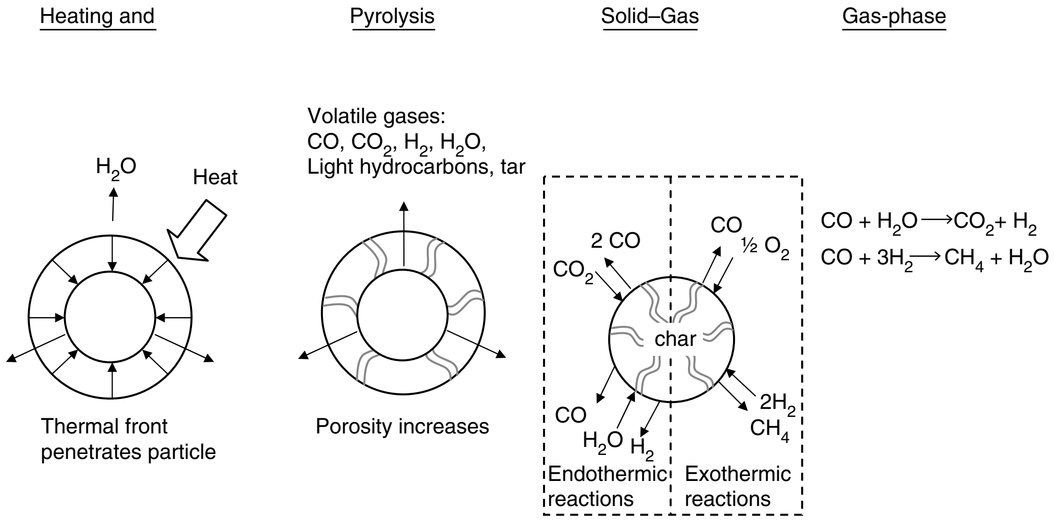

FIGURE 25.17 Processes of thermal gasification. (From Brown, R. C. 2003. *Biorenewable Resources: Engineering New Products from Agriculture*, Iowa State Press, Ames, IA.)

occurs and very high temperatures are produced. Although the gas flow is depleted of oxygen higher in the fuel bed, hot H_2O and CO_2 from combustion near the grate reduce char to H_2 and CO. These reactions cool the gas, but temperatures are still high enough to heat, dry, and pyrolyze the fuel moving down toward the grate. Of course, pyrolysis releases both condensable and non-condensable gases, and the producer gas leaving an updraft gasifier contains large quantities of tars on the order of 50 g/m^3. As a result, updraft gasifiers are generally not strong candidates for biomass energy applications.

In downdraft gasifiers, fuel and gas move in the same direction. Downdraft gasifiers appear to have been developed near the end of the nineteenth century, after the introduction of induced draft fans allowed air to be drawn downward through a gasifier in the same direction as the gravity-fed fuel. As shown in Figure 25.18b, contemporary designs usually add an arrangement of tuyeres that admit air or oxygen directly into a region known as the throat where combustion forms a bed of hot char. This design assures that condensable gases released during pyrolysis are forced to flow through the hot char bed, where tars are cracked. The producer gas is relatively free of tar (<1 g/m^3), making it a satisfactory fuel for engines. A disadvantage is the need for tightly controlled fuel properties (particles sized to between 1 and 30 cm, low ash content, and moisture less than 30%). Another disadvantage is a tendency for slagging or sintering of ash in the concentrated oxidation zone. Rotating ash grates or similar

TABLE 25.22 Producer Gas Composition from Various Kinds of Gasifiers

	Gaseous Constituents (vol% dry)						Gas Quality	
Gasifier type	H_2	CO	CO_2	CH_4	N_2	HHV (MJ/m^3)	Tars	Dust
Air-blown updraft	11	24	9	3	53	5.5	High (~10 g/m^3)	Low
Air-blown downdraft	17	21	13	1	48	5.7	Low (~1 g/m^3)	Medium
Air-blown fluidized bed	9	14	20	7	50	5.4	Medium (~10 g/m^3)	High
Oxygen-blown downdraft	32	48	15	2	3	10.4	Low (~1 g/m^3)	Low
Indirectly-heated fluidized bed	31	48	0	21	0	17.4	Medium (~10 g/m^3)	High

Source: From Milne, T. A., Abatzoglou, N., and Evans, R. J. 1998. Biomass Gasifier "Tars": Their Nature, Formation, and Conversion, National Renewable Energy Laboratory Report, NREL/TP-570-25357; Bridgwater, A. V., *Fuel*, 74, 631–653, 1995.

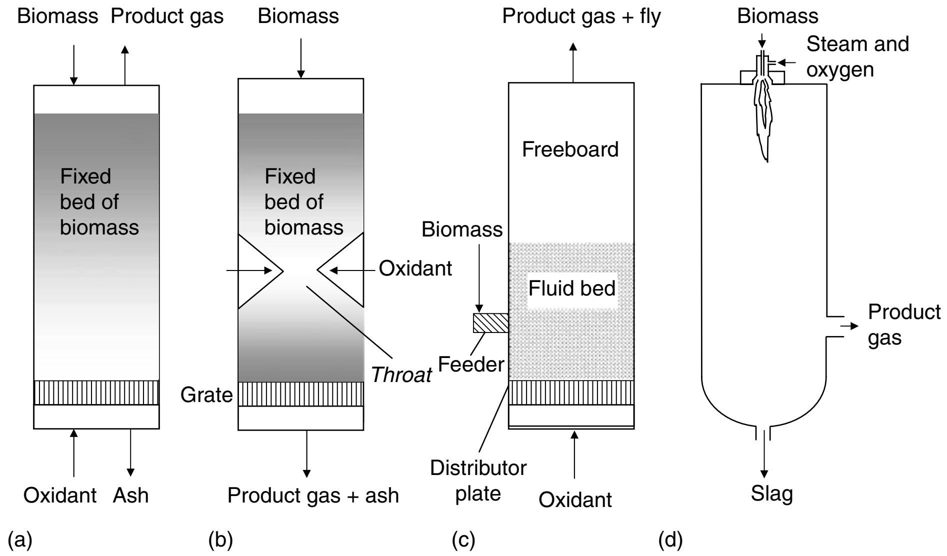

FIGURE 25.18 Types of biomass gasifiers: (a) updraft, (b) downdraft, (c) fluidized bed, (d) entrained flow. (From Brown, R. C., *Biorenewable Resources: Engineering New Products from Agriculture*, Iowa State Press, Ames, IA, 2003.)

mechanisms can solve this problem. Furthermore, incorporation of a throat region limits the maximum size of downdraft gasifiers to about 400 kg/h.

In a fluidized bed gasifier, illustrated in Figure 25.18c, a gas stream passes vertically upward through a bed of inert particulate material to form a turbulent mixture of gas and solid. Fuel is added at such a rate that it is only a few percent by weight of the bed inventory. Unlike the updraft and downdraft gasifiers, no segregated regions of combustion, pyrolysis, and tar cracking exist. The violent stirring action makes the bed uniform in temperature and composition with the result that gasification occurs simultaneously at all locations in the bed. Typically, a fluidized gasifier operates in the range of 700°C–850°C. By injecting fuel in the base of the bed, much of the tar can be cracked within the fluidized bed. However, a large insulated space above the bed, known as the freeboard, is usually included to promote additional tar cracking as well as more complete conversion of char. Nevertheless, tar production is intermediate between updraft and downdraft gasifiers (about 10 g/m^3). Fluidized beds are attractive for biomass gasification. They are able to process a wide variety of fuels including those with high moisture content and small particle size. They are easily scaled to large sizes suitable for electric power production. Disadvantages include relatively high power consumption to move gas through the fluidized bed; high exit gas temperatures, which complicates efficient energy recovery; and relatively high particulate burdens in the gas due to the abrasive forces acting within the fluidized bed.

A fourth kind of gasifier, illustrated in Figure 25.18d, employs finely pulverized fuel in an entrained flow reactor. This reactor was developed for steam-oxygen gasification of coal at temperatures of 1200°C–1500°C. These high temperatures assure excellent char conversion (approaching 100%) and low tar production and convert the ash to molten slag, which drains from the bottom of the reactor. The technology is attractive for advanced coal power plants but has not been widely explored for biomass because of the expense of finely dividing biomass, the difficulty of reaching high temperatures with biomass, and the presence of alkali in biomass, which leads to severe ash sintering. Despite these difficulties, entrained flow reactors are being considered for gasification of pretreated biomass (such as char and pyrolysis liquids).[13]

The fuel/air ratio is the single most important parameter for determining gasifier performance. Downdraft gasifiers can have better conversion efficiency and producer gas quality than fluidized bed gasifiers because they utilize a higher fuel/air ratio. Fluidized bed gasifiers, on the other hand, can generally handle a wider range of biomass feedstocks with higher moisture content.

Recent research in biomass gasification has focused on improving the heating value of product gas. Conventional gasification admits sufficient air or oxygen to the reactor to burn part of the fuel, thus releasing heat to support pyrolysis of the rest of the fuel. Gas produced in air-blown biomass gasifiers typically has heating value that is only 10%–20% than that of natural gas. This low heating value is largely the result of nitrogen diluting the fuel gas. Oxygen can be used as the fluidization agent, but high capital costs preclude this from consideration at the relatively small sizes envisioned for most biomass energy systems.

Indirectly heated gasification can improve gas-heating value by physically separating combustion and pyrolysis.[12] As a result, the products of combustion do not appear in the fuel gas. Higher heating values of 14,200 kJ/m^3 or higher are expected. Several schemes have been suggested for transporting heat from the combustion reactor to the pyrolysis reactor. These include transferring hot solids from the combustor to the pyrolyzer, transferring a chemically regenerative heat carrier between two reactors, transferring heat through a wall common to the reactors, and storing heat in high-temperature phase-change material.

Depending on the kind of gasifier, product gas can be contaminated by tar and particulate matter. Tar cannot be tolerated in many downstream applications, including internal combustion engines, fuel cells, and chemical synthesis reactors. Tar can deposit on surfaces in filters, heat exchangers, and engines where they reduce component performance and increase maintenance requirements. A well-designed gasifier has a high temperature zone through which pyrolysis products pass, allowing tars to thermally decompose ("crack") into the low molecular gases predicted by equilibrium theory. The production of particulate matter, a combination of ash and unreacted char from the biomass, varies considerably from one type of gasifier to another. Particulate matter can also deposit on critical power system components, degrading performance even at relatively low concentrations in some machinery.

Gas cleaning usually involves separate processes for removing solid particles and tar vapor or droplets. A gas cyclone operated above the condensation temperature for the least volatile tar constituent can remove most ash and char particles larger than about 5 μ in diameter. If removal of finer particles is required, then additional filtration such as ceramic candle filters or moving bed granular filters is required.

Two approaches are available for removing tar from product gas.[11] Scrubbing the gas stream with a fine mist of water or oil removes both tar and particles from the gas stream. Gas scrubbers are widely used in the chemical industry and are relatively inexpensive. However, cooling the gas and removing organic compounds reduce both sensible energy and chemical energy, which decreases overall energy conversion efficiency. Gas scrubbing also produces a toxic stream of tar, which complicates waste disposal.

The other approach for removing tar converts it into low molecular weight compounds, which has the advantages of increasing the heating value of the producer gas while eliminating a waste disposal problem. This "cracking" of tar into CO and H_2 can be accomplished by raising the gas to temperatures exceeding 1000°C. Such high temperatures are not easily achieved in most biomass gasifiers. The use of catalysts allows tar cracking to occur at much lower temperatures, in the range of 600°C–800°C. The gas is passed through a packed bed reactor containing catalyst with steam or oxygen sometimes used to promote reaction.

The thermodynamic efficiency of gasifiers is strongly dependent on the kind of gasifier and how the product gas is employed.[12] Some high-temperature, high-pressure gasifiers are able to convert 90% of the chemical energy of solid fuels into chemical and sensible heat of the product gas. However, these high efficiencies come at high capital and operating costs. Most biomass gasifiers have conversion efficiencies ranging between 70 and 80%. In some applications, such as process heaters or driers, both the chemical and sensible heat of the product gas can be utilized. In many power applications, though, the hot product gas must be cooled before it is utilized; thus, the sensible heat of the gas is lost. In this case, "cold gas" efficiency can be as low as 50%–60%. Whether the heat removed from the product gas can be recovered for other applications, like steam raising or fuel drying, ultimately determines which of these conversion efficiencies is most meaningful. Gas cleaning to remove tar and particulate matter also has a small negative impact on gasifier efficiency since it removes flammable constituents from the gas (tar and char particles) and generally requires a small amount of energy to run pumps.

25.2.5 Stirling Cycle

The Stirling cycle is an example of an external combustion engine; that is, the products of combustion do not come into contact with the fluid that undergoes the thermodynamic processes of the cycle.[14] In this respect, it resembles the Rankine steam cycle although its thermodynamic efficiency is theoretically higher than that of the Rankine cycle operating on the same fuel. In practice, the efficiencies of Stirling engines are relatively modest as are their output power, typically no more than a few kilowatts. They continue to attract attention mainly because of their low maintenance, high tolerance to contaminants, and relatively low pollution emissions. However, high costs have prevented significant market entry.

25.2.6 Rankine Cycle

The Rankine cycle is another example of an external combustion cycle.[15] As illustrated in Figure 25.19, fuel is burned in a furnace where the released heat is transferred to pressurized water contained within steel tubes. Steam generated in this process is expanded in a steam turbine, which drives an electric generator to produce electric power.

The Rankine steam power cycle has been the foundation of stationary power generation for over a century. Although Brayton cycles employing gas turbines and electrochemical cycles based on fuel cells will constitute much of the growth in power generation in the future, steam power plants will continue to supply the majority of electric power for decades to come and will find new applications in combination with advanced generation technologies. The reason for the Rankine cycle's preeminence has been its ability to directly fire coal and other inexpensive solid fuels. Constructed at scales of several hundred megawatts, the modern steam power plant can convert 35%–40% of chemical energy in fuel to electricity at a cost of $0.02–$0.05/kilowatt.

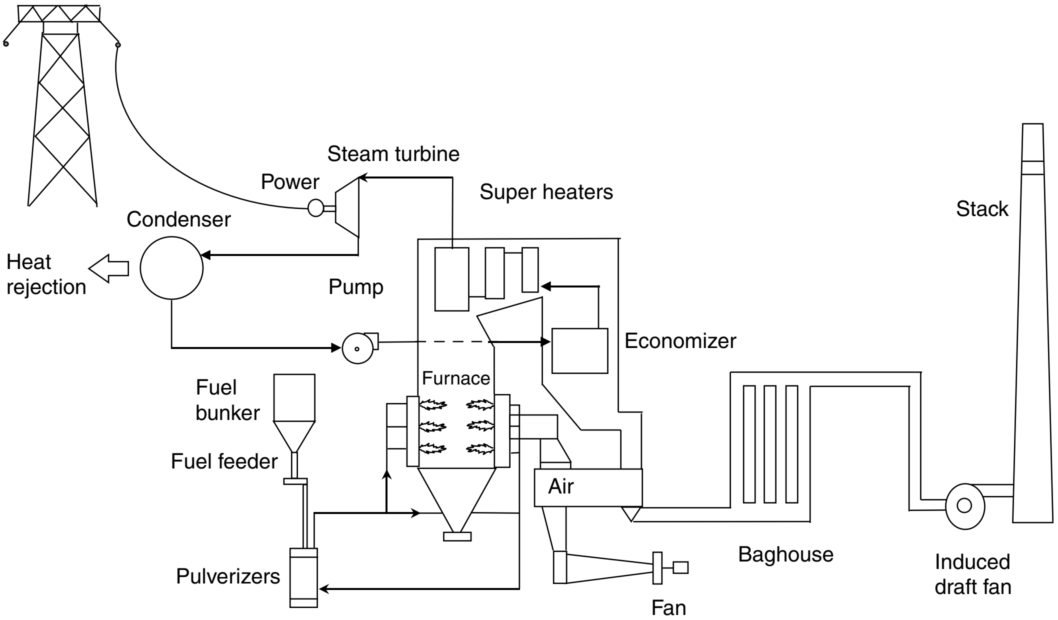

FIGURE 25.19 Rankine steam power plant. (From Brown, R. C., *Biorenewable Resources: Engineering New Products from Agriculture*, Iowa State Press, Ames, IA, 2003.)

Utility-scale steam power plants are not expected to dominate future growth in electric power infrastructure in the U.S. These giant plants take several years to plan and construct, which decreases their financial attractiveness in increasingly deregulated power markets. Coal and other fossil fuels burned in these plants are major sources of air pollution, including sulfur and nitrogen oxides, both of which are precursors to acid rain and the latter an important factor in smog formation; fine particulate matter, which is implicated in respiratory disease in urban areas; and heavy metals, the most prominent being mercury, which accumulates in the biosphere to toxic levels. Substitution of biorenewable resources such as wood and agricultural residues for coal in existing power plants could substantially reduce pollution emissions, although these plants are so large that the locally available biomass resources could supplant only a small fraction of the total energy requirement. Small-scale steam power plants sized for use of local biomass resources have low thermodynamic efficiencies, on the order of 25%, making them wasteful of energy resources.

25.2.7 Brayton Cycle

The Brayton cycle produces electric power by expanding hot gas through a turbine.[16] These gas turbines operate at temperatures approaching 1300°C compared with inlet temperatures of less than 650°C for steam turbines used in Rankine cycles. Although this difference in inlet temperature would suggest that Brayton cycles have much higher thermodynamic efficiencies than Rankine cycles, the Brayton cycle also has much higher exhaust temperature than does the Rankine cycle. Gas turbine exhaust temperatures are in the range of 400°C–600°C whereas steam turbine exhaust temperatures are on the order of 20°C. Furthermore, Brayton cycles, which contain both a gas compressor and gas turbine, have more sources of mechanical irreveribilities, further degrading thermodynamic efficiencies, which may only be marginally higher than the best Rankine steam cycles. However, improvements in gas turbine technology that allow operation at higher temperatures and pressures are expected to increase Rankine cycle efficiency for large power plants to greater than 50%, although 30% is more realistic for gas turbines sized appropriately for biomass power plants.

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

Gas turbines are well suited to gaseous and liquid fuels that are relatively free of contaminants that rapidly erode or corrode turbine blades. In this respect, gas turbine engines are not suitable for directly firing most biomass fuels. Solid biomass releases significant quantities of alkali metals, chlorine, mineral matter, and lesser amounts of sulfur upon burning. These would be entrained in the gas flow entering the expansion turbine where they would quickly contribute to blade failure. Cleaning large quantities of hot fuel gas is not generally considered as an economical proposition. Even the gas released from anaerobic digestion contains too much hydrogen sulfide to be directly burned in a gas turbine without first chemically scrubbing the gas to remove this corrosive agent.

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

25.2.8 Fuels Cells

Among the most exciting new energy technologies are fuel cells, which directly convert chemical energy into work, thus, bypassing the restriction on efficiency imposed by the Carnot relationship.[17] This does not imply that fuel cells can convert 100% of chemical enthalpy of a fuel into work, as the process still must conform to the laws of thermodynamics. In practice, irreversibilities limit their conversion efficiencies to 35%–60%, depending upon the fuel cell design. Thus, fuel cells can produce significantly more work from a given amount of fuel than can heat engines. However, carbonaceous fuels must first be reformed to hydrogen before they are suitable for use in fuel cells. The energy losses associated with fuel reforming must be included when determining the overall fuel-to-electricity conversion efficiency of a fuel cell.

The gas mixture produced by a biomass gasifier contains dust and tar that must be removed or greatly reduced for most applications, including power generation in fuel cells. Removal of tar would ideally be performed at elevated temperatures. If the gas is to be used in fuel cells, further cleaning is required to remove ammonia (NH_3), hydrogen chloride (HCl), and hydrogen sulfide (H_2S).[18] To obtain high-energy efficiency, trace contaminant removal must be performed at elevated temperatures for fuel cells that operate at relatively high temperatures. Low temperature fuel cells cannot tolerate CO, which can be removed by the water–gas shift reaction. The catalysts that facilitate the shift reaction, however, are poisoned by trace contaminants, which must be removed prior to the shift reactors. One method for removing H_2S and HCl is the use of a fixed bed of calcined dolomite or limestone and zinc titanate at temperatures around 630° C. This is followed by steam reforming at high temperature (750°C–850°C) to destroy tar and ammonia.[19]

25.2.9 Combined Cycles

In an effort to enhance energy conversion efficiency, combined cycle power systems have been developed, which recognize that waste heat from one power cycle can be used to drive a second power cycle.[20] Combined cycles would be unnecessary if a single heat engine could be built to operate between the temperature extremes of burning fuel and the ambient environment. However, temperature and pressure limitations on materials of construction have prevented this realization. Combined cycles employ a topping cycle operating at high temperatures and a bottoming cycle operating on the rejected heat from the topping cycle. Most commonly, combined cycle power plants employ a gas turbine engine for the topping cycle and a steam turbine plant for the bottoming cycle, achieving overall efficiencies of 60% or higher.

Clean-burning fuel from biomass for use in a combined cycle can be obtained by thermal gasification. Integrated gasification/combined cycle (IGCC) power is illustrated in Figure 25.20. Compressed air enters an oxygen plant, which separates oxygen from the air. The oxygen is used to gasify biomass in a pressurized gasifier to produce medium heating-value producer gas. The producer gas passes through cyclones and a gas clean-up system to remove particulate matter, tar, and other contaminants that may adversely affect gas turbine performance (alkali and chloride being the most prominent among these). These clean-up operations are best performed at high temperature and pressure to achieve high cycle efficiency. The clean gas is then burned in air and expanded through a gas turbine operating as a "topping" cycle. The gas exits the turbine at temperatures ranging between 400 and 600°C. A heat recovery steam generator produces steam for a "bottoming" cycle that employs a steam turbine. Electric power is produced at two locations in this plant, yielding thermodynamic efficiencies exceeding 47%.

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

An alternative to IGCC is to generate steam for injection into the gas turbine combustor, which increases mass flow and power output from the turbine. This variation, called a steam-injected gas turbine (STIG) cycle[20,21] is less capital intensive than IGCC, since it does not employ a steam turbine. The STIG cycle is commercially developed for natural gas; lower flammability limits for producer gas make steam injection more problematic for biomass-derived producer gas. The intercooled steam-injected gas turbine (ISTIG) is an advanced version of the STIG. This cycle further improves thermodynamic efficiency by cooling gas flow between several stages of compression (intercooling).

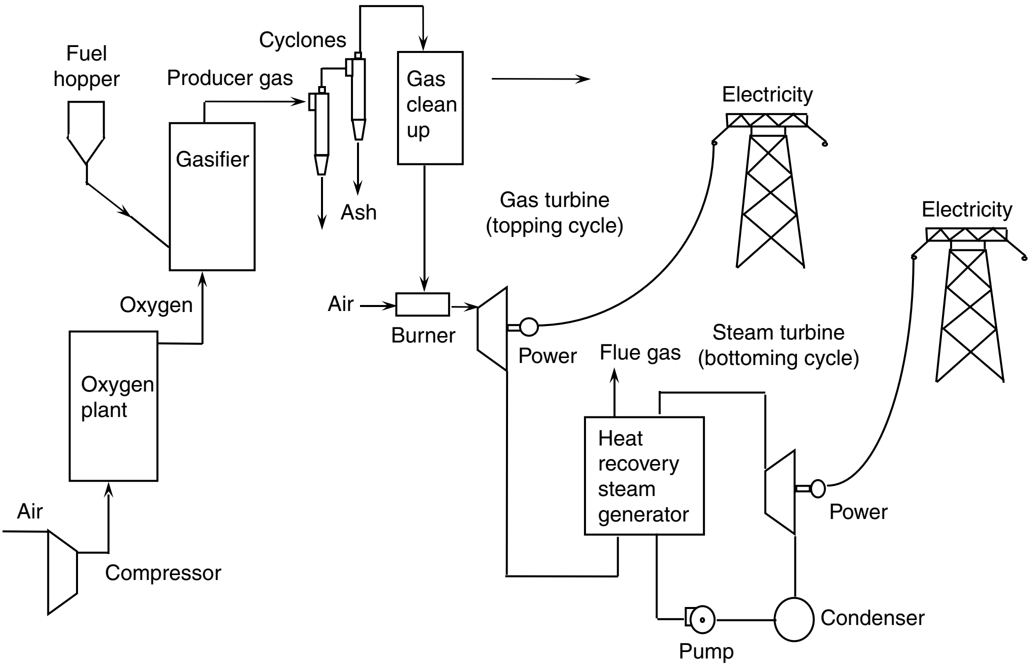

FIGURE 25.20 Integrated gasification/combined cycle power plant (IGCC) based on a gas turbine topping cycle. (From Brown, R. C., *Biorenewable Resources: Engineering New Products from Agriculture*, Iowa State Press, Ames, IA, 2003.)

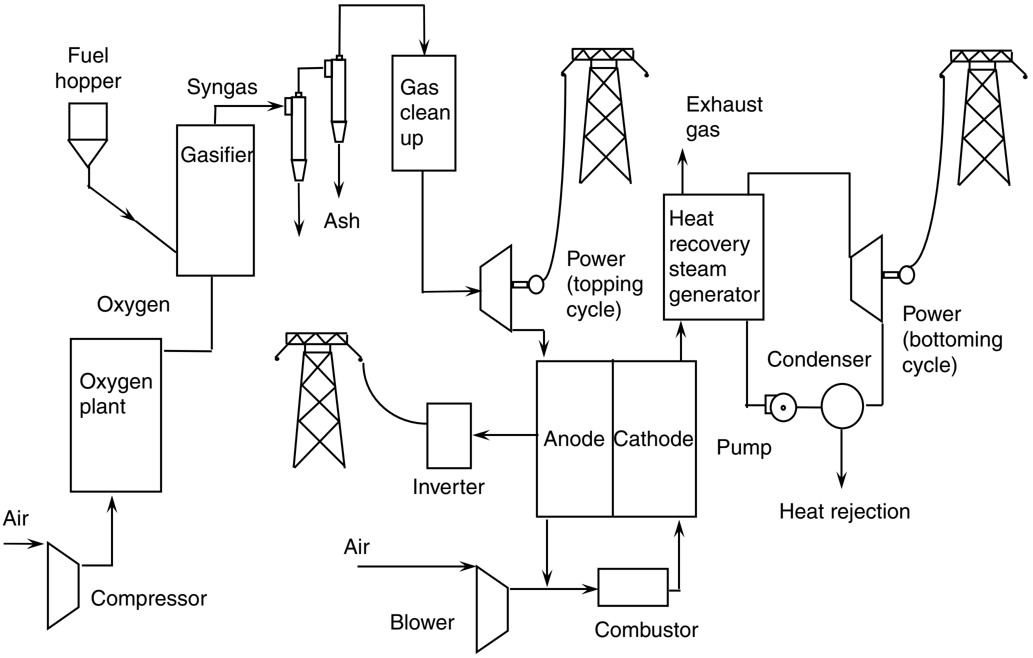

FIGURE 25.21 Combined cycle power plant based on high temperature fuel cells. (From Brown, R. C., *Biorenewable Resources: Engineering New Products from Agriculture*, Iowa State Press, Ames, IA, 2003.)

Figure 25.21 illustrates an IGCC power plant based on a molten carbonate fuel cell.[18] Biomass is gasified in oxygen to yield producer gas. Gasification occurs at elevated pressure to improve the yield of methane, which is important for proper thermal balance of this fuel cell. Hot-gas clean up to remove particulate matter, tar, and other contaminants is followed by expansion through a gas turbine as part of a topping power cycle. The pressure and temperature of the producer gas is sufficiently reduced after this to admit it into the fuel cell. High temperature exhaust gas exiting the cathode of the fuel cell enters a heat recovery steam generator, which is part of a bottoming cycle in the integrated plant. Thus, electricity is generated at three locations in the plant for an overall thermodynamic efficiency, reaching 60% or more.

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25.3 Biofuels

Robert C. Brown

25.3.1 Introduction

Almost 25% of energy consumption in the U.S. goes to transportation. More than half of this amount comes from imported petroleum. Thus, development of transportation fuels from biorenewable resources is a priority if decreased dependence on foreign sources of energy is to be achieved. Table 25.23 lists properties of both traditional and bio-based transportation fuels.[1–5]

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

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

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

Jet fuel is designated as either Jet A fuel or Jet B fuel. Jet A fuel is a kerosene type of fuel with relatively high flash point whereas Jet B fuel is a wide boiling range fuel, which more readily evaporates.

Bio-based transportation fuels, also known as biofuels, are currently dominated by ethanol and biodiesel. Ethanol, by virtue of its high octane number, is suitable for use in spark-ignition engines, while the high cetane numbers of biodiesel, which are methyl or ethyl esters formulated from vegetable or animal fats, make them suitable for use in compression-ignition engines. However, there are other candidate liquid biofuels including methanol, mixed alcohols, and Fischer–Tropsch (F–T) liquids, as well as gaseous biofuels including hydrogen, methane, ammonia, and dimethyl ether, which will also be discussed.

25.3.2 Ethanol

Ethanol can be produced by the fermentation of sugar or starch crops. A fuel ethanol market has been developed in Brazil based on sugarcane[6] while the U.S. has relied on cornstarch for commercial

TABLE 25.23 Comparison of Transportation Fuels

	Fossil Fuel-Derived		Biomass-Derived							
Fuel Type	Gasoline[1]	No. 2 Diesel Fuel[1]	Methanol[1]	Ethanol[1]	Methyl Ester[2] (from soybean oil)	Fischer–Tropsch A[2]	Hydrogen[3]	Methane[3]	Ammonia[4]	Dimethyl Ether[2]
Specific gravity [a]	0.72–0.78	0.85	0.796	0.794	0.886	0.770	0.071 (liq)	0.422 (liq)	0.682 (liq)	0.660
Kinematic viscosity at 20°C–25°C (mm^2/s)	0.8	2.5	0.75	1.51	3.9	2.08	105[b]	16.5[b]	14.7[c]	0.227
Boiling point range (°C)	30–225	210–235	65	78	339	164–352	−253	−162	−33.4[c]	−24.9
Flash point (°C)	−43	52	11	13	188	58.5		−184	—	—
Autoignition temperature (°C)	370	254	464	423	—	—	566–582	540	630	235
Octane no. (research)	91–100	—	109	109	—	—	>130	>120	110	—
Octane no. (motor)	82–92	—	89	90	—	—	—	—	—	—
Cetane no.	<15	37–56	<15	<15	55	74.6	—	—	—	>55
Heat of vaporization (kJ/kg)	380	375	1185	920	—	—	447	509	1371[c]	402[d]
Lower heating value (MJ/kg)	43.5	45	20.1	27	37	43.9	120	49.5	18.8	28.88

[a] Measured at 16°C except for liquefied gases, which are saturated liquids at their respective boiling points.

[b] Munson, B. et al. 1994. Table 1.6 *Fundamentals of Fluid Mechanics*, 2nd Ed., Wiley, NY.

[c] Perry, R. and Green, W. 1984. *Perry's Chemical Engineers' Handbook*, 6th Ed., McGraw-Hill, NY, chap. 3.

[d] Kajitani, S. et al. 1997. p. 35 of Engine Performance and Exhaust Characteristics of Direct-Injection Diesel Engine Operated with DME, Society of Automotive Engineers Inc.

production of fuel ethanol. Technologies are also being developed to convert lignocellulose into sugars or syngas, a mixture of carbon monoxide (CO) and hydrogen, either of which can be fermented into ethanol.

On a volumetric basis, ethanol has only 66% of the heating value of gasoline. Thus, the range of a vehicle operating on pure ethanol is theoretically reduced by a corresponding amount and, accordingly, meaningful comparisons of the cost of gasoline and ethanol should be made on the basis of energy delivered ($/GJ) instead of fuel volume ($/l). However, fuel economy depends on many complex interactions between a fuel and the combustion environment within an engine, which some argue improves the relative performance of ethanol.[7] For example, the higher octane number for ethanol compared to gasoline (109 vs. 91–101) allows engines to be designed to run at higher compression ratios, which improves both power and fuel economy. Estimates for efficiency improvements in engines optimized for ethanol instead of gasoline range from 15 to 20%, resulting in a driving range approaching 80% of that of gasoline.[8]

Internal combustion engines can be fueled on pure ethanol (known as neat alcohol or E100) or blends of ethanol and gasoline. Brazil employs 190 proof ethanol (95 vol% alcohol and 5% water), which eliminates the energy consuming step of producing anhydrous ethanol. In the United States two ethanol–gasoline blends are common, E85 contains 85% ethanol and 15% gasoline and E10 contains only 10% ethanol with the balance being gasoline. The advantage of E10 is that it can be used in vehicles with engines designed for gasoline; however, its use is accompanied by a loss in fuel economy (as measured in km/l or miles/gal) compared to gasoline, amounting to 2%–5%.[9]

A significant problem with ethanol–gasoline blends is water-induced phase separation. Water contaminating a storage tank or pipeline is readily absorbed by ethanol, resulting in a lower water-rich layer and an upper hydrocarbon-rich layer, which interferes with proper engine operation. Water contamination is a problem that has not been fully addressed by the refining, blending, and distribution industries; thus transportation of ethanol–gasoline blends in pipelines is not permitted in the United States and long-term storage is to be avoided.[10]

25.3.3 Ethanol from Starch Crops

Starch is a polymer that accumulates as granules in many kinds of plant cells where they serve as a storage carbohydrate. Mechanical grinding readily liberates starch granules. The hydrogen bonds between the basic units of maltose in this polymer are easily penetrated by water, making depolymerization, and solubilization relatively easy.

Hydrolysis, the process by which water splits a larger reactant molecule into two smaller product molecules, is readily accomplished for starch. Acid catalyzed hydrolysis in "starch cookers" at temperatures of 150°C–200°C proceeds to completion in seconds to minutes. In recent years, enzymatic hydrolysis has supplanted acid hydrolysis due to higher selectivity.

Starch is a glucose polymer with two main components: amylose, a liner polymer of glucose with alpha—1,4 linkages, and amylopectin, a branched chain including alpha—1,6 linkages at the branch points.[11] Thus, enzymatic saccharification of starch requires two enzymes. The enzyme amylase hydrolyzes starch to maltose in a process known as liquefaction. The enzyme maltase hydrolyzes maltose into glucose in a process known as saccharification. The consumption of either acid or enzymes for starch hydrolysis is less than 1:100 by weight, making the cost of hydrolysis only a small part of the cost of starch fermentation.

Cereal grains, such as corn, wheat, and barley, are the most widely used sources of starch for fermentation.[11] The cell walls of grains must be disrupted to expose starch polymers before they can be hydrolyzed to fermentable sugars (that is, monosaccharides and disaccharides). Grain starch consists of 10–20 wt% amylose and 80–90 wt% amylopectin, both of which yield glucose or maltose on hydrolysis. Although the amylose is water soluble, the amylopectin is insoluble, requiring a "cooking" operation to solubilize it in prior to hydrolysis.

Cereal grains also contain other components, such as protein, oil and fiber, which may be of sufficient value to recover along with the starch. For example, gluten, a mixture of plant proteins occurring in cereal grains, chiefly wheat and corn, is of value as an adhesive and animal feed. If these components are to be separately recovered, extensive pretreatment, known as wet milling, is required before the starch is hydrolyzed and fermented. Under some circumstances, separation of plant components is not economically justified; simpler dry grinding is employed to release starch polymers and the whole grain is fermented. Of the 12.9 gigaliters (3.4 billion gal) of fuel ethanol produced in the United States in 2004, about two-thirds was from dry grinding while the remaining one-third was from wet milling. The capital investment for dry milling is less than that for a comparably sized wet-milling plant. However, the higher value of its by-products, greater product flexibility, and simpler ethanol production can make a wet-milling plant a more profitable investment.

25.3.3.1 Dry Grinding of Corn

Dry grinding for ethanol production[12] uses a roller mill to grind grain into a meal, which exposes the starch. The meal is slurried with water to form a mash, which is cooked with enzymes to release sugars, followed by fermentation to ethanol. The fibrous residue remaining upon completion of fermentation is recovered from the base of the beer stripping column, mixed with yeast and other unfermented residues, and dried to a co-product known as distillers' dried grains and solubles (DDGS). This coproduct, containing about 25 wt% protein and residual oil, is a valuable feed for cattle. Profitability of a corn-to-ethanol plant is strongly tied to the successful marketing of DDGS A dry grind ethanol plant is illustrated schematically in Figure 25.22.[13]

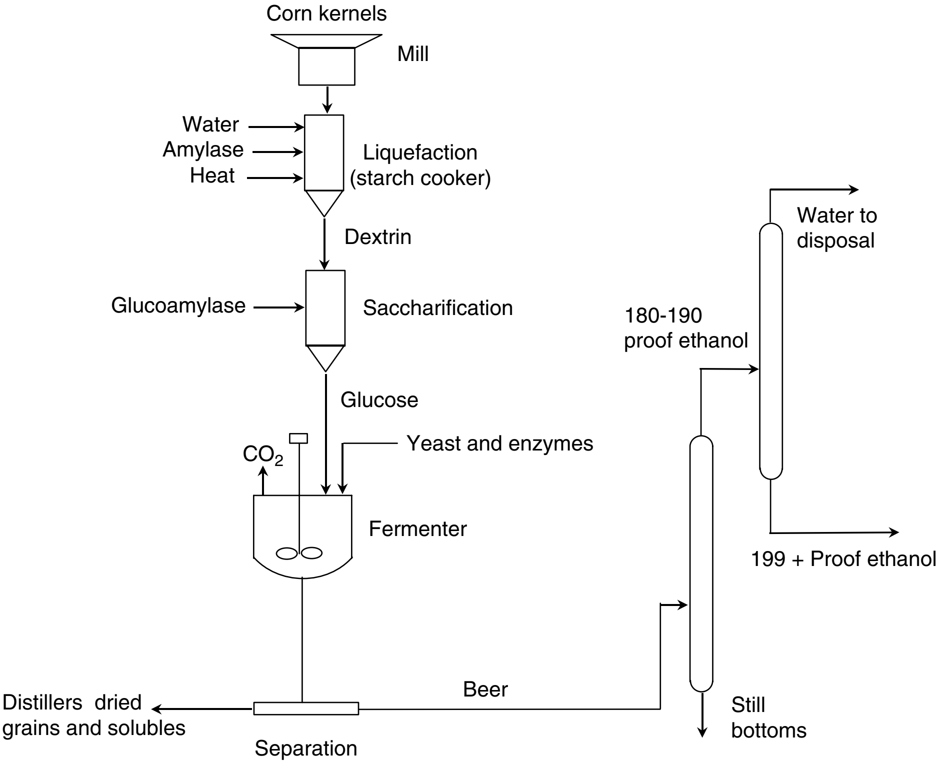


FIGURE 25.22 Dry grinding of corn. (From Brown, R. C., *Biorenewable Resources: Engineering New Products from Agriculture*, Blackwell Publishing, Ames, IA, 2003.)

A typical dry milling plant will produce about 9.5–9.8 L (2.5–2.6 gal) of ethanol per bushel of corn processed. Yields of co-products per bushel of corn are 7.7–8.2 kg (17–18 lb) of DDGS and 7.3–7.7 kg (16–17 lb) of carbon dioxide evolved from fermentation, the latter of which can be sold to the carbonated beverage industry. As a rule of thumb, the three products are produced in approximately equal weight per bushel, with each accounting for approximately one-third of the initial weight of the corn.

25.3.3.2 Wet Milling of Corn

Wet milling[14] has the advantage that it separates plant components into carbohydrate (starch), lipids (corn oil), a protein-rich material (gluten), and fiber (hulls). This gives a company access to higher value markets as well as provides flexibility in the use of starch as a food product or in the production of fuel ethanol.

The wet milling process is illustrated in Figure 25.23.[13] The corn is cleaned and then conveyed into steep tanks where it is soaked in a dilute solution of sulfur dioxide for 24–36 h, which swells and softens the corn kernels. Some of the protein and other compounds are dissolved in the resulting corn steep liquor, which represents an inexpensive source of nitrogen and vitamins.

After separating the corn from the steep liquor, the wet kernels are coarsely ground to release the hull and germ from the endosperm. Hydrocyclones or screens separate the germ from the rest of the components. After drying, oil is extracted from the germ by either solvents or a screw press, leaving a residual oil cake The hull and endosperm pass through rotating disc mills that grind the endosperm into fine fractions of starch and gluten while the hull yields coarser fiber particles, which can be screened out from the finer fractions. Centrifugal separators separate the lighter gluten from the starch.

The starch can be used directly as a food product or for industrial manufacturing processes, especially papermaking. The starch can also be converted to monosaccharides for the production of food or fuel, depending on relative market demand. Saccharification by amylase enzymes yields corn syrup, a glucose

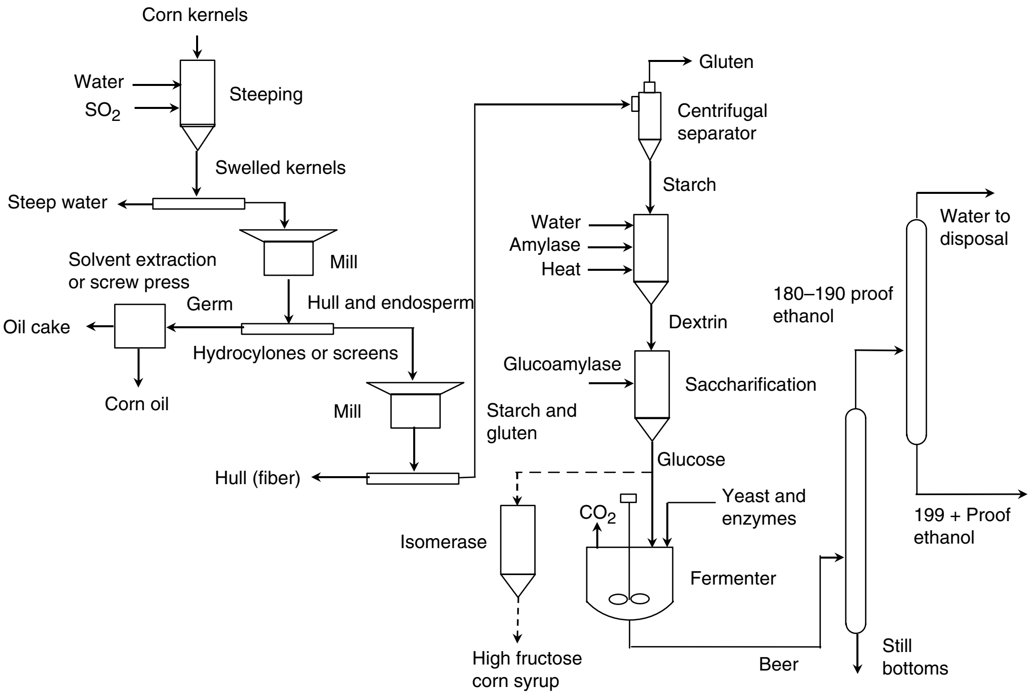


FIGURE 25.23 Wet milling of corn. (From Brown, R. C., *Biorenewable Resources: Engineering New Products from Agriculture*, Blackwell Publishing, Ames, IA, 2003.)

solution that can be directly fermented to fuel ethanol Alternatively, treated with isomerase enzymes, the glucose is partially converted to fructose to yield a liquid sweetener known as high fructose corn syrup (HFCS). In plants that can alternate between fuel ethanol and HFCS production, relatively more ethanol is produced in the winter while relatively more HFCS is produced in the summer.

The gluten product, known as corn gluten meal, contains 60% protein and is used primarily as poultry feed. The fiber from the hulls is combined with other by-products, such as the oil cake, steep water solubles, and excess yeast from stillage, dried and sold as corn gluten feed. Containing 21% or more of protein, it is primarily used as feed for dairy cattle.

A typical wet milling plant will produce 9.5–9.8 L (2.5–2.6 gal) of ethanol per bushel of corn processed. Yields of other coproducts per bushel of corn are 0.7 kg (1.7 lb) of corn oil, 1.4 kg (3 lb) of corn gluten meal (60% protein), 5.9 kg (13 lb) of corn gluten feed (21% protein), and 7.7 kg (17 lb) of carbon dioxide. Like dry milling, the three products of ethanol, feed, and carbon dioxide are produced in approximately equal weight per bushel, with each accounting for approximately one-third of the initial weight of the corn.

25.3.4 Ethanol from Lignocellulosic Feedstocks

Much of the carbohydrate in plant materials is structural polysaccharides, providing shape and strength to the plant. The hydrolysis of polysaccharides in cell walls is more difficult than the hydrolysis of storage polysaccharides like starch. This structural material, known as lignocellulose, is a composite of cellulose fibers embedded in a cross-linked lignin-hemicellulose matrix.[15] Depolymerization to basic plant components is difficult because lignocellulose is resistant to both chemical and biological attack.

A variety of physical, chemical, and enzymatic processes have been developed to fractionate lignocellulose into the major plant components of hemicellulose, cellulose, and lignin.[16] The hemicellulose fraction is readily hydrolyzed to pentoses (five carbon sugars) but pentoses are difficult to ferment. The cellulose exists as both amorphous and crystalline forms, which hydrolyze to hexoses (six carbon sugars). Crystalline cellulose is recalcitrant to hydrolysis. However, the resulting hexoses are readily fermented. Distillation can recover the desired products of fermentation. Lignin, which is not susceptible to biological transformation, can be chemically upgraded or, more frequently, simply burned as boiler fuel. The steps of pretreatment, hydrolysis, fermentation, and distillation in the production of bio-based products from lignocellulose are described in the following sections.

25.3.4.1 Pretreatment

Pretreatment is one of the most costly steps in conversion of lignocellulose to sugars, accounting for about 33% of the total processing costs.[17] Pretreatments often produce biological inhibitors, which impact the cost of fermenting the resulting sugars Accordingly, much attention is directed at developing low cost and effective pretreatments.

An important goal of all pretreatments is to increase the surface area of lignocellulosic material, making the polysaccharides more susceptible to hydrolysis. Thus, comminution, or size reduction, is an integral part of all pretreatments. Primary size reduction employs hammer mills to produce particles that can pass through 3 mm screen openings.

The mechanisms by which pretreatments improve the digestibility of lignocellulose are not well understood.[17] Pretreatment effectiveness has been correlated with removal of hemicellulose and lignin. Lignin solubilization is beneficial for subsequent hydrolysis, but may also produce derivatives that inhibit enzyme activity. Some pretreatments reduces crystallinity of cellulose, which improves reactivity, but this does not appear to be the key for many successfully pretreatments.

A large variety of pretreatment processes have been developed.[18] Biological pretreatments employ microorganisms that produce lignin-degrading enzymes (ligninase). Steam explosion involves saturation of the pores of plant materials with steam followed by rapid decompression; the explosive expansion of steam reduces the plant material to separated fibers, presumably increasing the accessibility of polysaccharides to subsequent hydrolysis. Ammonia fiber explosion (AFEX) is similar to steam explosion except that liquid ammonia is employed. It is very effective on agricultural residues but has not been successful in pretreating woody biomass.

25.3.4.2 Hydrolysis

Three basic methods for hydrolyzing structural polysaccharides in plant cell walls to ferment sugars that are available: concentrated acid hydrolysis, dilute acid hydrolysis, and enzymatic hydrolysis.[16,19] The two acid processes hydrolyze both hemicellulose and cellulose with very little pretreatment beyond comminution of the lignocellulosic material to particles of about 1 mm in size. The enzymatic process must be preceded by extensive pretreatment to separate the cellulose, hemicellulose, and lignin fractions.

Concentrated acid hydrolysis is based on the discovery over a century ago that carbohydrates in wood will dissolve in 72% sulfuric acid at room temperature, leaving behind the lignin fraction. For fermentation, the solution of oligiosaccharides is diluted to 4% H_2SO_4, and heated at the boiling point for four hours, or in an autoclave at 120°C for one hour to yield monosaccharides. Following neutralization with limestone, the sugar solution can be fermented. Concentrated acid hydrolysis is relatively simple and is attractive for its high sugar yields, which approach 100% of theoretical hexose yields.

Dilute acid hydrolysis (about 1% acid by weight) greatly reduces the amount of acid required to hydrolyze lignocellulose. The process is accelerated by operation at elevated temperatures: 100°C–160°C for hemicellulose and 180°C–220°C for cellulose. Unfortunately, the high temperatures cause oligiosaccharides released from the lignocellulose to decompose, greatly reducing yields of simple sugars to only 55%–60% of the theoretical yield. The decomposition products include a large number of microbial toxins, such as acetic acid and furfural, which inhibit fermentation of the sugars. The need for corrosion resistant equipment and low concentrations of sugars from some reactor systems also adversely impact the cost of sugars.

Enzymatic hydrolysis was developed to utilize both cellulose and hemicellulose better from lignocellulosic materials. Pretreatment solubilizes hemicellulose under milder conditions than those required for acid hydrolysis of cellulose. Subsequent enzymatic hydrolysis of the cellulose does not degrade pentoses released during prehydrolysis. Cellulose is a homopolysaccharide of glucose linked by β-1,4$'$-glycosidic bonds. Thus, enzymatic hydrolysis of cellulose proceeds in several steps to break glycosidic bonds by the action of a system of enzymes known as cellulase. The system of enzymes also usually contains hemicellulase to hydrolyze any hemicellulose not solubilized by prehydrolysis.

25.3.4.3 Fermentation

Simultaneous saccharification and fermentation (SSF) has been developed for fermenting sugars released from lignocellulose.[16,19] The SSF process combines hydrolysis (saccharification) and fermentation to overcome end product inhibition that occurs during hydrolysis of cellobiose. By combining hydrolysis and fermentation in the same reactor, glucose is rapidly removed before it can inhibit further hydrolysis. The SSF process is illustrated in Figure 25.24.[13] The biomass feedstock is milled and then prehydrolyzed to yield a mixture of pentoses, primarily xylose and arabinose, and fiber. The mixture is neutralized with limestone and mixed with cellulase and hemicellulase enzymes, which are either purchased commercially or produced on site, yeast, and nutrients. The cellulose and any remaining hemicellulose are solubilized to hexose (glucose) and pentoses (xylose and arabinose), which are immediately fermented to ethanol. The rate-limiting step is the hydrolysis of cellulose to glucose. The optimum temperature for the hydrolysis/fermentation reactor is a compromise between the optimum temperature for cellulase activity and the best temperature for the yeast. Lignin is separated from the mixture and used as boiler fuel.

The beer is distilled to ethanol in a process identical to that employed after sugar or starch fermentations. Energy consumption in the distillation process is partly responsible for criticism that ethanol production consumes more energy than it produces. Although there is basis for this criticism in older plants, modern plants pay close attention to energy consumption. Some plants are reported to use as little as 5.6 MJ of steam per liter of ethanol produced, with a total energy consumption of

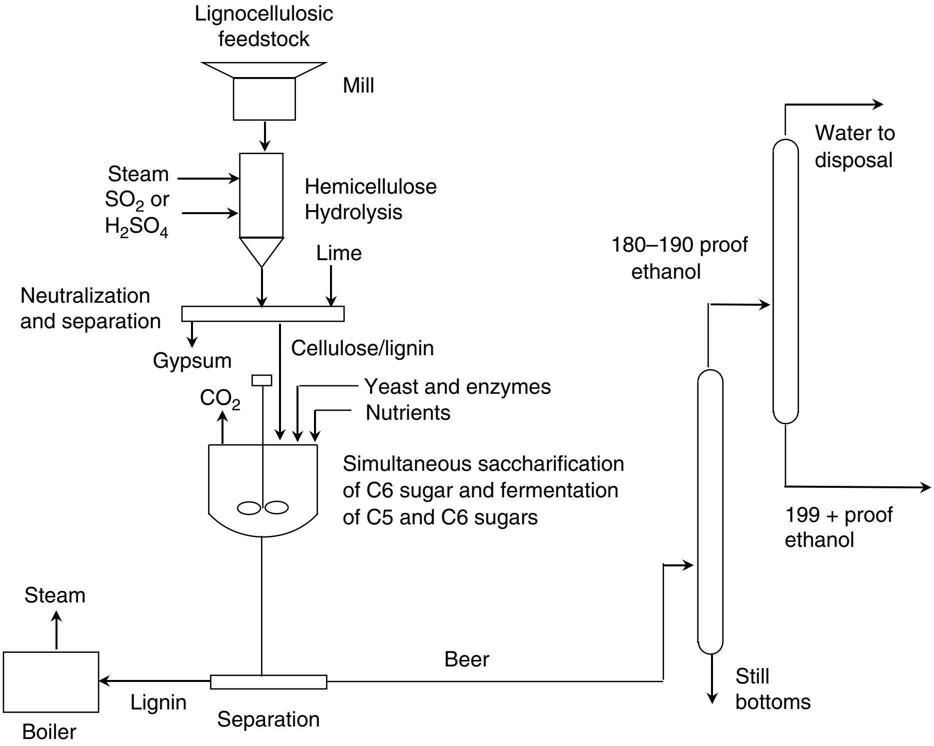


FIGURE 25.24 Enzymatic hydrolysis of lignocellulosic biomass. (From Brown, R. C., *Biorenewable Resources: Engineering New Products from Agriculture*, Blackwell Publishing, Ames, IA, 2003.)

11.1–12.5 MJ/L of product ethanol. A recent analysis of energy usage in corn-to-ethanol plants is found in Ref. 20.

25.3.5 Biodiesel

Vegetable oils, which are triglycerides of fatty acids, have been recognized long as potential fuels in diesel engines. Compared to petroleum-based diesel fuels, vegetable oils have higher viscosity and lower volatility, which results in fouling of engine valves and less favorable combustion performance, especially in direct-injection engines.[21] The solution to this problem is to convert the triglycerides into methyl esters or ethyl esters of the fatty acids, known as biodiesel, and the by-product 1,2,3-propanetriol (glycerol).

Table 25.23 illustrates that fuel properties of biodiesel are very similar to petroleum-based diesel. Only the specific gravity and viscosity of biodiesel are slightly higher than for diesel while the cetane numbers and heating values are comparable. Significantly higher flash points for biodiesel represent greater safety in storage and transportation. Biodiesel can be used in unmodified diesel engines with no excess wear or operational problems. Tests in light and heavy trucks showed few differences other than a requirement for more frequent oil changes because of the build-up of ester fuel in engine crankcases.[21]

Triglycerides, also known as fats and oils, are esters of glycerol and fatty acids, which are long-chain carboxylic acids containing even numbers of carbon atoms.[22] 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.

A wide variety of plant species produce triglycerides in commercially significant quantities, most of it occurring in seeds.[23] Average oil yields range from 150 L/ha for cottonseed to 814 L/ha for peanut oil although intensive cultivation might double these numbers. Soybeans are responsible for more than 50% of world production of oilseed, representing 48–82 million bbl/year. However, the Chinese tallow tree, cultivated in the southern U.S., has the potential for several fold higher productivity than soybeans and is particularly attractive for its ability to grow on saline soils that are not currently used for agriculture.

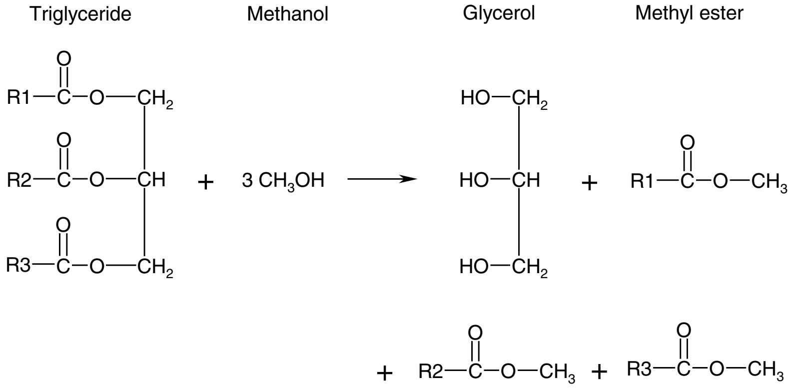
Extraction of seed oil is relatively straightforward. The seeds are crushed to release the oil from the seed. Mechanical pressing is used to extract oil from seeds with oil content exceeding 20%. Solvent extraction is required for seeds of lower oil content. The residual seed material, known as meal,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

Triglycerides are also recovered as a coproduct of the pulping of pinewood by the kraft process.[24] The esters of both fatty and resin acids are saponified to sodium salts and recovered as soap foam on the surface of the black (pulping) liquor. These salts are acidified to form a mixture of 30% fatty acids, 35% resin acids, and 35% unsaponifiable esters known as tall oil.

Microorganisms, including yeasts, fungi, and algae are also potential sources of triglycerides.[25] Anaerobic yeasts and fungi accumulate triglycerides during the latter stages of growth when nutrients other than carbon begin to be exhausted. Algae, which grow over a wide range of temperatures in high-salinity water, can produce as much as 60% of their body weight as lipids when deprived of key nutrients such as silicon for diatoms or nitrogen for green algae. They employ relatively low substrate concentrations, in the order of 10–40 g/L. Unlike ethanol production, product recovery is relatively simple because of the sequestration of the oil in the algae. One suggestion is to build algae ponds in the desert Southwest United States where inexpensive flat land, water from alkaline aquifiers, and carbon dioxide from power plants could be combined to generate triglyceride-based fuel.

The higher viscosity and lower volatility of triglycerides compared to diesel fuel leads to coking of the injectors and rings of diesel engines. Chemical modification of triglycerides to methyl or ethyl esters yields excellent diesel-engine fuel. Biodiesel is the generic name given to these modified vegetable oils and animal fats. Suitable feedstocks include soybean, sunflower, cottonseed, corn, groundnut (peanut), safflower, rapeseed, waste cooking oils, and animal fats. Waste oils or tallow (white or yellow grease) can also be converted to biodiesel.

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.[26] For example, one triglyceride molecule reacts with three methanol molecules to produce one molecule of 1,2,3-propanetriol (glycerol) and three ester molecules:



$$\mathrm{R1{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}CH_2,\ R2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}CH,\ R3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}CH_2 + 3\,CH_3OH \longrightarrow HO{-}CH_2,\ HO{-}CH,\ HO{-}CH_2 + R1{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}CH_3 + R2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}CH_3 + R3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}CH_3} \tag{25.14}$$

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

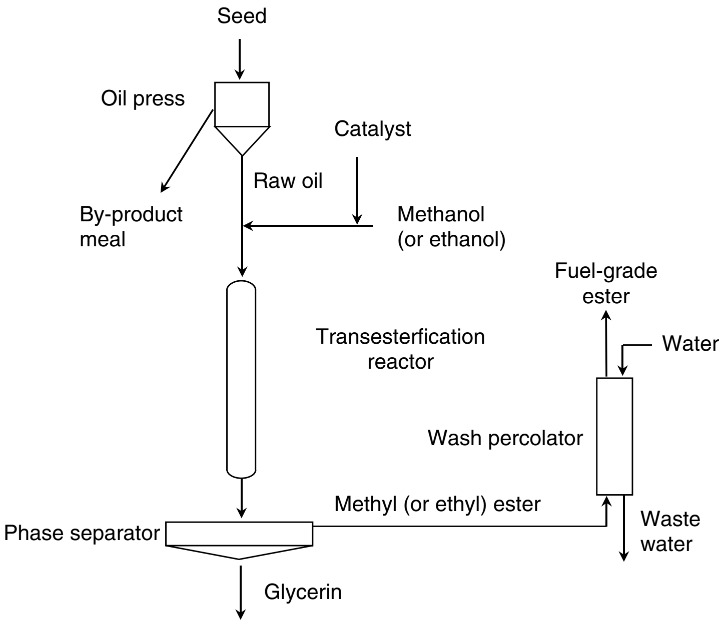


FIGURE 25.25 Conversion of triglycerides to methyl (or ethyl) esters and glycerol. (From Brown, R. C., *Biorenewable Resources: Engineering New Products from Agriculture*, Blackwell Publishing, Ames, IA, 2003.)

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 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 25.25.[13]

25.3.6 Transportation Fuels from Biomass-Derived Syngas

The producer gas resulting from gasification can be used to manufacture a variety of liquid transportation fuels including methanol, ethanol, mixed alcohols, and F–T liquids. It can also be used to produce hydrogen (H_2), methane (CH_4), dimethyl ether (CH_3OCH_3), and ammonia (NH_3), which are gaseous compounds at ambient conditions but can be compressed or liquefied for use as transportation fuels. A relatively pure mixture of CO and hydrogen is usually preferred for synthesizing these compounds. Since raw producer gas can also contain various amounts of light hydrocarbons, tar, particulate matter, and trace contaminants, such as sulfur, chlorine, and ammonia, some downstream treatment of the gas stream may be required to produce the desired proportions of CO and H_2.

25.3.6.1 Methanol from Syngas

As shown in Table 25.23, the fuel properties of methanol are similar to those of ethanol: narrow boiling point range, high heat of vaporization, and high octane number. It has only 49% of the volumetric heating value of gasoline. As a transportation fuel, it has many of the same advantages and disadvantages as ethanol.

Methanol is formed by the exothermic reaction of one mole of CO with two moles of hydrogen:[27]

$$CO + 2H_2 \rightarrow CH_3OH \tag{25.15}$$

Low temperatures and high pressures thermodynamically favor the production of methanol. Current commercial operations use a fixed catalytic bed operated at 250°C and 60–100 atmospheres with gas recycle to remove the large amount of heat released by this exothermic reaction. More recently, liquid phase slurry reactors have been introduced to improve contact between syngas and catalyst as well as enhance the removal of heat from the reactor.

Biomass gasification does not necessarily yield the H_2/CO ratio of 2.0 required for methanol synthesis. Hydrogen enrichment can be achieved by passing syngas and steam over a catalytic bed, which promotes the water–gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (25.16)$$

Low temperatures thermodynamically favor this exothermic reaction. To obtain satisfactory reaction rates, catalysts are employed in one or more fixed bed reactors operated in the temperature range of 250°C–400°C.

However, methanol is considerably more toxic than ethanol. Recent rulings banning the closely related and similarly toxic fuel additive methyl tertiary butyl ether (MTBE) from many states because of groundwater contamination makes methanol an unlikely replacement for gasoline.

25.3.6.2 Alcohols from Syngas

25.3.6.2.1 Catalytic

Efforts in Germany during World War II to develop alternative motor fuels discovered that iron-based catalysts could yield appreciable quantities of water soluble alcohols from syngas, especially ethanol:[28]

$$CO + 3H_2 \rightarrow CH_3CH_2OH \qquad (25.17)$$

These early efforts yielded liquids containing as much as 45%–60% alcohols of which 60%–70% was ethanol. Working at pressures of around 50 bar and temperatures in the range of 220°C–370°C, researchers have developed catalysts with selectivity to alcohols of over 95%, but production of pure ethanol has been elusive.

Because the product typically contains a mixture methanol, ethanol, 1-propanol, and 2-propanol, some researchers have advocated the use of "mixed alcohols" as transportation fuels. One advantage is the ability to use lower H_2:CO ratios than is required for methanol or F–T synthesis:[29]

$$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O \qquad (25.18)$$

with n typically ranging from 1 to 8. The process was commercialized in Germany between 1935 and 1945 but eventually abandoned because of the increased availability of inexpensive petroleum. An extensive review of mixed alcohol synthesis technology is found in Ref. 30.

An alternative approach to obtaining neat ethanol from syngas is to first synthesize methanol and subsequently react this product with additional syngas:[31]

$$CH_3OH + 2CO + H_2 \rightarrow CH_3CH_2OH + CO_2 \qquad (25.19)$$

Direct carbonylation of methanol has the advantage of yielding ethanol without coproduct water, which would eliminate energy-intensive distillations. The cost-effectiveness of this approach to ethanol synthesis has not been proven.

25.3.6.2.2 Biological

Certain microorganisms, are known as unicarbontrophs, able to grow on one carbon compounds as the sole source of carbon and energy.[32] Acetogens can convert CO or mixtures of CO and H_2 to fatty acids and, in some cases, alcohols. *Clostridium Ijungdahli*, a gram-positive, motile, rod-shaped anaerobic bacterium isolated from chicken waste, has received particular attention for its ability to co-metabolize

CO and H_2 to form acetic acid (CH_3COOH) and ethanol (CH_3CH_2OH). The wild-type strain of *C. ljundahlii* produced an ethanol-to-acetate ratio of only 0.05 with maximum ethanol concentration of 0.1 g/L. This ratio is very sensitive to acidity; in decreasing pH to 4.0 and increased the ratio to 3.0. Other adjustments to the culture media and operating conditions nearly eliminated acetate production and increased ethanol concentration to 48 g/L after 25 days.

This gasification/fermentation route to bio-based fuels from lignocellulosic feedstocks has several advantages compared to hydrolytic/fermentation techniques.[33] Gasification allows very high conversion of feedstock to usable carbon compounds (approaching 100%) whereas hydrolysis only recovers about half the lignocellulose as fermentable sugars. Gasification yields a uniform product (a gaseous mixture of CO, CO_2, and H_2) regardless of the biomass feedstock employed whereas hydrolysis yields a product dependent on the content of cellulose, hemicellulose, and lignin in the feedstock. Finally, since the syngas is produced at high temperatures, gasification yields an inherently aseptic carbon supply for fermentation.

Biological processing of syngas has several advantages compared to chemical processing.[33] The H_2/CO ratio is not critical to biological processing of syngas, thus making unnecessary the water–gas shift reaction to increase the hydrogen content of biomass-derived syngas. Whereas catalytic syngas reactors require high temperatures and pressures, biocatalysts operate near ambient temperature and pressure. Also, biocatalysts are typically more specific than inorganic catalysts.

Syngas fermentation faces several challenges before commercial adoption.[33] Syngas bioreactors exhibit low volumetric productivities due, in part, to low cell densities. Cell recycle or immobilization of cells in the bioreactor are possible solutions to this problem. Mass transfer of syngas into the liquid phase is also relatively slow. In commercial-scale aerobic fermentations, mass transfer of oxygen is generally the rate limiting process. The problem will be exacerbated for syngas fermentations since the molar solubility of CO and H_2 are only 77% and 65% of that of oxygen, respectively. Dispersion of syngas into microbubbles of 50 μm diameter will be important to successful design of multiphase bioreactors.

25.3.6.3 Fischer–Tropsch Liquids

Production of hydrocarbons from syngas can be directly accomplished by F–T synthesis, which reacts and polymerizes syngas to light hydrocarbon gases, paraffinic waxes, and alcohols according to the generalized reaction:[30]

$$CO + 2H_2 \rightarrow -CH_2- + H_2O \tag{25.20}$$

Additional processing can produce diesel fuel and gasoline. Both methanol synthesis and F–T synthesis require careful control of the H_2/CO ratio to satisfy the stoichiometry of the synthesis reactions as well as to avoid deposition of carbon on the catalysts (coking). An optimal H_2/CO ratio of 2:1 is maintained through the water–gas shift reaction (Equation 25.16). Product distributions are functions of temperature, feed gas composition (H_2/CO), pressure, catalyst type, and catalyst composition. Depending on the types and quantities of F–T products desired, either low (200°C–240°C) or high temperature (300°C–350°C) synthesis is used with either an iron (Fe) or cobalt catalyst (Co).

The technology was extensively developed and commercialized in Germany during World War II when it was denied access to petroleum-rich regions of the world. Likewise South Africa, faced with a world oil embargo during their era of apartheid, employed F–T technology to sustain its national economy. A comprehensive bibliography of F–T literature can be found on the Web.[34]

25.3.6.4 Gaseous Transportation Fuels

The ideal transportation fuel is a stable liquid at ambient temperature and pressure that can be readily vaporized and burned within an engine. However, some gaseous compounds are also potential transportation fuels if their density can be substantially increased by compression. Among these gaseous transportation fuels are hydrogen, methane, ammonia, and dimethyl ether.

Hydrogen can be manufactured from syngas via the water–gas shift reaction (Equation 25.16). This moderately exothermic reaction is best performed at relatively low temperatures in one or more stages with the aid of catalysts. Although this might be one of the most cost-effective ways to produce hydrogen fuel, the physical characteristics of hydrogen present challenges in its use as transportation fuel In particular, its low density even under cryogenic or high pressure conditions limits on-board storage of this fuel. Its wide flammability range also presents unique safety problems in its use in transportation systems.[35]

Methane can be coaxed to be the main product of gasification in a process known as hydrogasification:[36]

$$C + 2H_2 \rightarrow CH_4 \tag{25.21}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{25.22}$$

These exothermic reactions require low temperatures, high pressures, and large quantities of hydrogen to favor complete conversion to methane. Thus, the process requires separate generation of hydrogen and catalysts to achieve reasonable reaction rates. It has been demonstrated at the commercial scale using coal as the carbonaceous fuel. Although more easily pressurized or liquefied than hydrogen, its density is still too low to be an attractive transportation fuel except in some urban mass transit applications.[37]

Anhydrous ammonia (NH_3) is a gas at ambient conditions but is readily liquefied at room temperature by storage at 10 bars pressure, achieving 87% of the density of gasoline.[4] In fact, it has nearly the same density, boiling point, and octane number as propane, which has been widely employed as a portable fuel source.

Ammonia is produced by the Haber process at 200 bar and 500°C[38]:

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{25.23}$$

As a widely employed agricultural fertilizer, the United States already has in place production, storage, and distribution infrastructure for its use.

Ammonia has been tested as fuel in spark ignition engines, diesel engines, and gas turbines. In tests dating back to the 1960s, near theoretical performance was achieved with ammonia if it was partially dissociated to achieve 1% hydrogen concentration at the engine intake.[39] Somewhat surprising for this nitrogen-rich fuel, nitrogen oxide emissions were lower than those obtained from octane fuel. Because of its lower heating value, an ammonia-fueled vehicle would require a fuel tank about 2.4 times larger than for a propane-fueled vehicle.

Dimethyl ether, like liquefied petroleum gas (LPG) is a non-toxic, flammable gas at ambient conditions that is easily stored as a liquid under modest pressures.[40] It is currently used as an aerosol propellant in the cosmetic industry, but has excellent potential as a fuel for heating, cooking, and power. It is particularly attractive as a substitute for petroleum-based diesel fuel since it has comparable cetane number but yields essentially zero particulate emissions and low NO_x emissions. It is produced either directly from syngas or indirectly through the dehydration of methanol by reactions at high pressure over catalysts. Of course, this syngas route also allows it to be produced from fossil fuels, and much of the current interest in this alternative fuel arises from the possibility of manufacturing it from inexpensive stranded natural gas.

25.3.6.5 Energy Return from Renewable Fuels

Some researchers have expressed concern that renewable fuels return less energy than the fossil energy used to produce them. This criticism has been particularly leveled against grain ethanol but more recently the energy return on any biomass-derived transportation fuel has come into question. The ratio of energy returned to fossil fuel invested is defined as:

$$R_E = \frac{E_{out}}{E_{f,in}} \tag{25.24}$$

where E_{out} = energy content of a unit of motor fuel, $E_{f,in}$ = fossil energy input to produce a unit of motor fuel.

Some authors[41] refer to this ratio as the "energy return on investment," but this name is more commonly associated with another kind of energy ratio subsequently described.

Notice that this definition is not equivalent to the classical energy efficiency for a thermodynamic process:

$$\eta = \frac{E_{out}}{E_{in}} \tag{25.25}$$

where E_{out} = energy content of a unit of motor fuel, E_{in} = energy input (both fossil and renewable) to produce a unit of motor fuel.

Neither should it be confused with energy return on investment (EROI), first introduced in the 1950s as a way to account for all the energy expended in the manufacture of an energy product, including the energy to extract, transport, process, and distribute the product, an accounting now incorporated into a life cycle assessment[42]:

$$\text{EROI} = \frac{E_{out}}{E_{M,\ in}} \tag{25.26}$$

where E_{out} = energy content of a unit of energy product, $E_{M,in}$ = energy consumed to manufacture a unit of energy product (excluding chemical enthalpy of feedstock).

The concept was originally formulated to compare the energy consumed in the manufacture of various kinds of durable and non-durable goods. For this purpose it provides a useful alternative to standard economic evaluations for decision making. However, when the concept was applied to energy products, such as electricity and motor fuels, the chemical enthalpy of the feedstock was not included in the EROI calculation. The chemical enthalpy of a fuel is usually the single largest energy input in its processing; thus, the advantage of fossil fuels compared to renewable fuels is often overstated in EROI comparisons because the production of energy products from fossil fuels often consume relatively smaller amounts of energy in their manufacture (this is particularly true for petroleum and natural gas).

The R_E is preferred when evaluating how effective an energy product is in displacing fossil fuels and reducing greenhouse gas emissions. An $R_E > 0.76–0.81$ (the range for the refining of gasoline) indicates at least some nominal advantage over petroleum-derived fuels while an $R_E > 1$ indicates that more "renewable" energy in the form of motor fuel was produced than fossil fuel was consumed in its production.

A large number of studies have investigated R_E in the production of ethanol from corn grain. Wang[43] summarized these results as a function of year of publication. As shown in Figure 25.26, R_E has been climbing over the years, but there is considerable scatter in the values. These values range from 0.44 to 2.1. Averaging over the values reported by 14 *different* study groups (to avoid replicating values of the same study groups reported in different publications) yields an energy ratio of 1.3. The differences appear largely to arise over disagreements on the amount of fertilizer applied to corn crops, the yield of corn crops, the ethanol yield from corn, and the amount of process heat required within ethanol plants.[44] In general, higher E_R values can be expected from large, modern ethanol plants. In comparison, the E_R for production of gasoline from petroleum is only 0.76–0.81.[41]

Evaluations of R_E for cellulosic ethanol manufacture are less common. Hammerschlag[41] reports that three studies found $r_E > 4.4$ while only one study, by Pimentel and Patzek,[45] report r_E to be as low as 0.69. This discrepancy appears to arise from Pimentel and Patzek's assumption that fossil fuels rather than

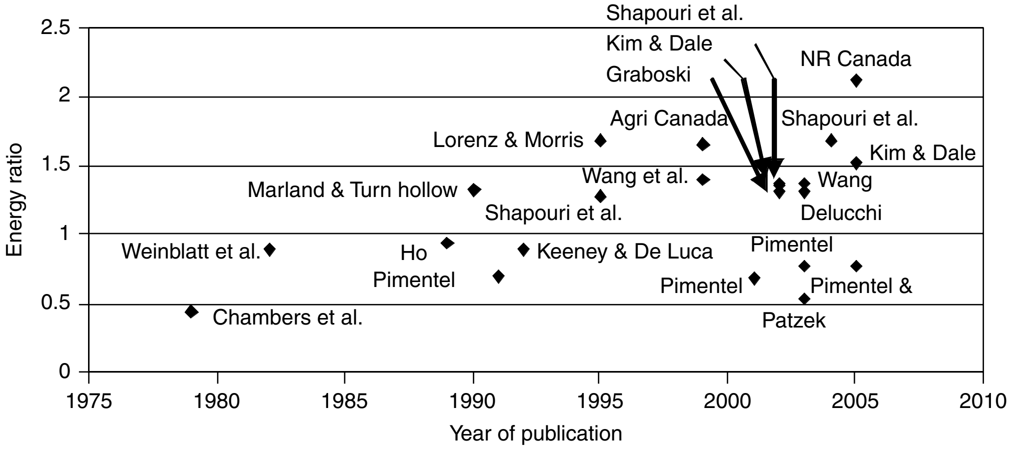


FIGURE 25.26 ER values reported by various investigators over a twenty-five year interval. (Adapted from Wang, W., *NGCA Renewable Fuels Forum*, National Press Club, Australia, August 23, 2005.)

lignin by-product will be used for process heat in the cellulose ethanol plant. With proper energy integration, R_E will likely exceed 4.4 in the production of ethanol from cellulose.

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