Bioenergy
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Chapter 16

Biomethane from Biomass, Biowaste, and Biofuels

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Biofuel production from agricultural, municipal, and industrial wastes is efficiently accomplished through conversion to biogas, a mixture of mostly methane (CH_4) and carbon dioxide (CO_2), via anaerobic digestion. Anaerobic digestion is a process by which a complex mixture of symbiotic microorganisms transforms organic materials under oxygen-free conditions into biogas, nutrients, and additional cell matter, leaving salts and refractory organic matter. In practice, microbial anaerobic conversion to methane is a process for both effective waste treatment and sustainable energy production. In waste treatment, this process can provide a source of energy while reducing the pollution and odor potential of the substrate. Unlike fossil fuels, use of renewable methane represents a closed carbon cycle and thus does not contribute to increases in the atmospheric concentration of carbon dioxide (Wilkie, 2005).

Microbial methane production has the potential for reducing the demand for fossil fuels like coal, oil, and natural gas that have provided the power for developing and maintaining the technologically advanced modern world. However, fossil resources are finite, and their continued recovery and use significantly impact our environment and affect the global climate. Shortages of oil and gas are predicted to occur within our lifetimes or those of our children. To prepare for a transition to more sustainable sources of energy, viable alternatives for conservation, supplementation, and replacement must be explored, posthaste.

Biogas production from agricultural, municipal, and industrial wastes can contribute to sustainable energy production, especially when nutrients conserved in the process are returned to agricultural production (Fig. 1). Little energy is consumed in the process, and consequently the net energy from biogas production is high compared to other conversion technologies. The technology for methane production is scalable and has been applied globally to a broad range of organic waste feedstocks, most commonly animal manures (Wilkie et al., 2004). However, methane production is not limited to conversion of animal manures. Biogas can be made from most biomass and waste materials regardless of the composition and over a large range of moisture contents, with limited feedstock preparation. The feedstocks for this omnivorous process can be composed of carbohydrates, lignocellulosics, proteins, fats, or mixtures of these components. The process is suitable for conversion of liquid, slurry, and solid wastes; it can even be employed for the conversion of gaseous combustion products (synthesis gas) from thermochemical gasification systems. In addition, methane production can be effectively applied to improve energy yields from other biofuel production processes including bioethanol, biodiesel, and biohydrogen production. Implementation of digestion technology at agricultural, municipal, and industrial facilities allows efficient decentralized energy generation and distribution to local markets. While traditionally applied to wastes and wastewaters, the anaerobic digestion of energy crops can also be employed in a sustainable bioenergy system.

ANAEROBIC MICROBIOLOGY

Methane is the end product of anaerobic metabolism—a metabolic sequence carried out by communities of hydrolytic bacteria and fungi, acid-producing intermediary organisms, and finally, methanogenic *Archaebacteria*. Methane-producing communities are very stable and resilient, but they are also complex and largely undefined.

Buswell and Sollo (1948) demonstrated the treatability of a range of wastes and emphasized the concept of an acid phase versus a methane phase, showing the importance of volatile organic acids as intermediates in the process. They also demonstrated the applicability of a stoichiometric equation that balanced carbon, hydrogen, and oxygen (equation 1) to predict the amount

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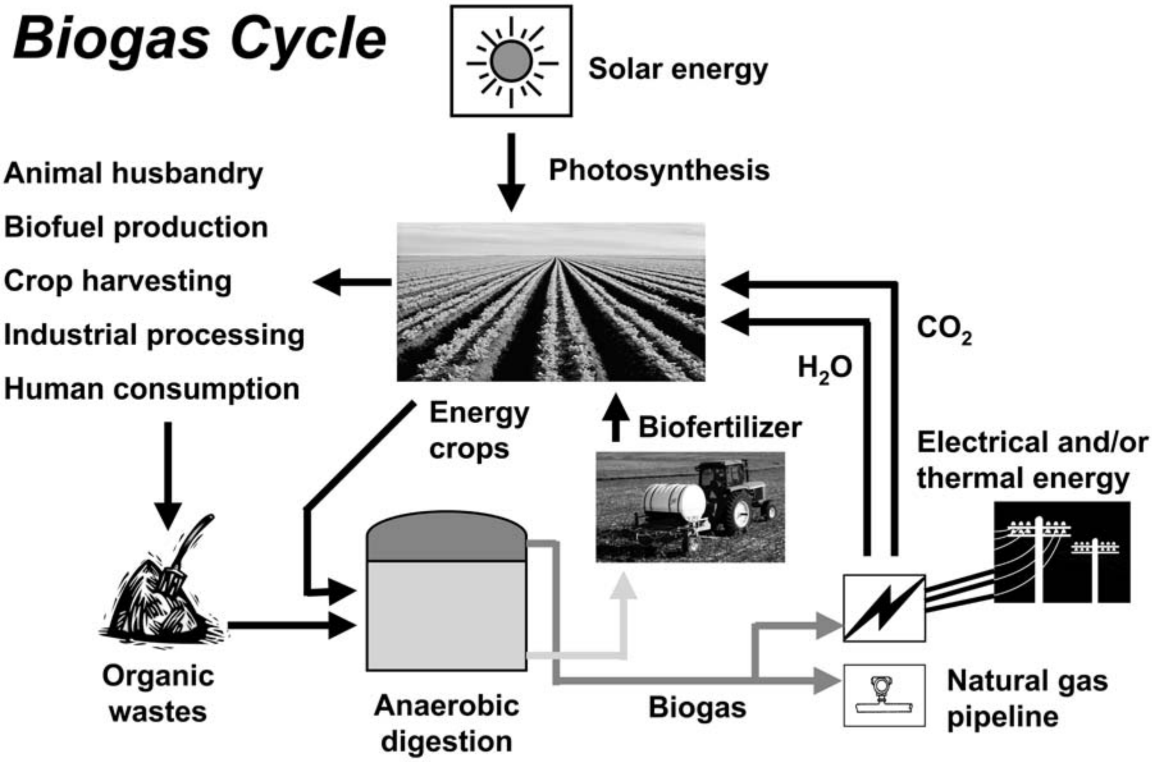

Figure 1. Biogas cycle

of methane and carbon dioxide evolved from conversion of organic compounds with a known empirical formula. Later, ^{14}C tracers were used to show that acetate was indeed cleaved to form methane and carbon dioxide, suggesting that acids were important intermediates in the conversion process.

$$C_nH_aO_b + (n - a/4 - b/2)H_2O \rightarrow (n/2 - a/8 + b/4)CO_2 + (n/2 + a/8 - b/4)CH_4 \quad (1)$$

Of great importance to the understanding of anaerobic microbiology was the discovery of Bryant et al. (1967), through isolating the elusive “S-organism” from *Methanobacterium omelianskii*, that the conversion of ethanol to methane was accomplished with a mixed culture. The discovery of other cocultures quickly followed, and the number of species isolated in pure culture increased. With the identification of closely coupled syntrophic cocultures of methanogens and other species, the earlier hypothesis of an acid phase followed by a methanogenic phase developed into a more descriptive scheme that embraces the importance of hydrogen as an intermediate in the process.

First the fermentative, or hydrolytic, bacteria and fungi hydrolyze complex organic polymers and ferment them to organic acids, hydrogen (or formate), and carbon dioxide. The hydrogen-producing acetogenic bacteria ferment the larger acids to a combination of acetic acid, one-carbon compounds, hydrogen, and carbon dioxide. The homoacetogenic bacteria synthesize acetic acid by utilizing hydrogen/carbon dioxide or one-carbon compounds or by hydrolyzing multicarbon compounds.

The methanogenic *Archaebacteria* uniquely catabolize acetic acid and one-carbon compounds to methane. The methanogens are obligate anaerobes that can pick up electrons from dead-end fermentations, through interspecies hydrogen transfer, and shuttle these electrons through a unique form of respiration which results in the reduction of carbon dioxide to methane. The organisms that use hydrogen to reduce CO_2 are commonly regarded as the earliest life forms due to their chemoautotrophic abilities.

All morphological forms are represented among the methanogens including rods, cocci, spirals, sarcinae, and filamentous organisms. Surprisingly, this diverse group of organisms is known to metabolize a very limited number of substrates including acetate, formate, methanol, acetone, methylamines, carbon monoxide, and H_2/CO_2. The substrates for methanogenesis divide these organisms into groups, two of which are notably important in active digesters: the aceticlastic methanogens, which cleave acetic acid, and the hydrogen-utilizing methanogens, which utilize hydrogen and one-carbon compounds. However, this distinction is not always useful since some species may metabolize both substrates.

For aceticlastic methanogens, low levels of acetate (<50 mg/liter) favor the growth of more-filamentous organisms (e.g., *Methanosaeta*) that must rely on a larger surface-to-volume ratio in order to improve substrate diffusion rates. High levels of acetate favor the predominance of clusters of aceticlastic methanogens (e.g., *Methanosarcina*), which have lower surface-to-volume ratios that serve to protect them from the inhibitory nature of high organic acid concentrations. Differences in maximum growth rate and substrate utilization affinities can be exploited to select for predominant methanogens. Organisms such as *Methanosarcina* should be favored for selection if high conversion rates of high-strength wastes are the primary goal, whereas *Methanosaeta* should be favored if low effluent biochemical oxygen demand is more important. In addition, these attributes can be exploited together by staging an anaerobic process with the first stage favoring high conversion rates and the next stage favoring effluent quality.

PROCESS

In practice, anaerobic digestion is the engineered methanogenic decomposition of organic matter, carried out in reactor vessels, called digesters, that may be mixed or unmixed and heated or unheated. The process uses a mixed culture of ubiquitous organisms, and due to its mixed-culture nature, there are no requirements for feedstock sterilization and no contamination concerns. Stable digester operation requires that the bacterial groups be in dynamic equilibrium, as some of the intermediate metabolites (hydrogen, propionate, ammonia, and sulfide) can be inhibitory and the pH of the system must remain near neutral. Also, methane is sparingly soluble, such that end product recovery is efficient and economical as the gas separates itself from the aqueous phase and is easily removed from the digester through piping that conveys it to storage for final use.

Current commercial-scale methods of methane production yield from 50 to 97% conversion of substrate to methane on an energy basis, depending on the feedstock. The mean oxidation state of the feedstock determines the stoichiometry of the end products. Carbohydrate substrates yield 50% methane and 50% carbon dioxide, while more-reduced feedstocks (e.g., lipids) yield higher proportions of methane. The theoretical methane yield of carbohydrates, proteins, and fats is given in Table 1. Also, carbohydrate-rich substrates yield more methane than do feedstocks with high concentrations of lignocellulose.

Table 1. Theoretical methane yield of biomass components

Component	Methane yield (liter/g of VS)
Carbohydrates	0.35
Proteins (leucine)	0.57
Fats (lauric acid)	0.95

The natural assemblages in the mixed culture have evolved to form robust and stable cultures with extremely broad substrate utilization capabilities. There is no requirement for genetically modified organisms to extend catabolic activity, so sterilization of process residuals is not necessary. Although the free energy available from anaerobic conversion of substrates to methane is low, causing low microbial-growth rates, the activity and turnover rates of substrates are higher than for aerobic metabolism. Also, anaerobic respiration of methanogens results in the production of a noninhibitory product, methane, that moves into the gaseous phase, which contrasts with other fermentation processes that produce inhibitory final products (e.g., ethanol) that remain in solution. This gives the process a distinct advantage for either continuous or batch conversion of substrates to energy products.

Of significance for the application of anaerobic digestion is the high level of energy recovery in the biogas compared to the energy content of the substrate utilized. The efficiency of this conversion is directly related to the low level of free energy of reaction available for microbial synthesis. Rather than transforming the energy in waste into sludge as in aerobic processes, a minimal amount of this energy is consumed by anaerobic cell synthesis and the rest is retained in the methane end product. This also explains the low rates of microbial growth in anaerobic systems compared to aerobic processes.

Chemical oxygen demand (COD) is a convenient measurement to estimate the organic content in a wastewater or biomass sample and, theoretically, 0.35 liter of methane is formed from 1 g of COD digested. In aerobic processes such as the activated-sludge process, the sludge yield can be as high as 0.5 kg of dry solids per kg of COD utilized, whereas the sludge yields for anaerobic processes range from 0.03 to 0.15 kg of dry solids per kg of COD consumed depending on the substrate. Sludge by-product from aerobic processes requires further treatment for stabilization in order to reduce odor and pollution potential. Furthermore, after stabilization, the sludge still requires final disposal. Anaerobic treatment processes, in contrast, produce a relatively small amount of sludge by-product which is more stable, less capable of causing odor or pollution problems, and ready for final disposition in sustainable crop production. Also, anaerobic treatment results in pathogen decimation through microbial competition and starvation.

Nutrients contained in the organic matter are conserved and mineralized to more soluble and biologically available forms, providing a more predictable biofertilizer. Since sludge production in anaerobic digestion is minimal, virtually all of the nitrogen and phosphorus contained in the original waste is retained in the treated effluent. By recycling the treated effluents back to productive agricultural lands at appropriate rates, the crops benefit from the presence of these important plant nutrients. Where insufficient cropland is available, other nutrient recovery technologies may be employed to reduce the nutrient content of the digested wastewater.

DESIGNS

The construction of anaerobic digesters for biogas production has little in common with that of industrial fermentors. The low value of energy products compared with fermentation products necessitates low-cost construction and materials. While industrial fermentation vessels are often jacketed stainless steel tanks, with baffles, agitators, and clean-in-place systems, and constructed on elevated stands, anaerobic digesters are often simple insulated concrete or carbon steel tanks constructed with low-cost materials either on or below the surface. Without the need for efficient aeration, the requirement for mixing must only meet the needs for microbial contact with substrate, uniform temperature, and prevention of solids accumulation. Since sterility is not a concern, no clean-in-place systems or provisions to prevent microbial contamination are required. Unlike other fermentations, no specific process or equipment is required for product recovery, since methane is relatively insoluble and therefore separates spontaneously.

Anaerobic digesters must be essentially gas-tight vessels with a provision for introducing feedstock and removing effluent and biogas. The classical anaerobic digester is essentially a chemostat. Tanks with rigid tops must have provisions for pressure and vacuum relief, and biogas piping must meet safety standards. Tank tops may also be floating rigid tops or flexible membrane materials. Simple heat exchangers may be placed internally or external to the tank, and mixing can employ agitators, simple recirculation of the mixed liquor, or injection of compressed biogas.

There are two broad classifications of digesters, those that rely on suspended growth of microorganisms and those that employ a mechanism for immobilization to retain active microbial biomass within the vessel. With feedstocks containing high levels of suspended solids, nonimmobilized designs are generally used including covered anaerobic lagoons, complete-mix reactors, plug-flow reactors, and anaerobic contact reactors. These digesters require relatively long hydraulic retention times (HRT) of 15 to 60 days and moderate organic loading rates (OLR), typically expressed as weight of organic matter (volatile solids [VS] or COD) per culture volume of reactor per day. The maximum OLR and minimum HRT that can be applied are dependent on operating temperature, waste characteristics, and reactor type.

Feeds with low concentrations of suspended solids (<2%) can be digested in high-rate immobilized reactors such as the upflow anaerobic sludge-bed digester (UASB), anaerobic filter (AF), and fixed-film systems. These reactors retain high concentrations of immobilized microorganisms, permit low HRT without organism washout, and are particularly suited for treatment of soluble wastewaters. The tendency of microbial consortia to adhere to surfaces and grow as a biofilm spurred the development of both the aerobic trickling filter and the AF reactor (also called a packed bed). While the principle of filling a reactor with a packing media is straightforward, the selection of packing material and operational strategies may have significant effects on performance and costs. Media used for packing have included natural materials such as stones, clay, wood, bamboo, and reeds, as well as polymers made of polyvinyl chloride, polyethylene, and polypropylene. Polymers shaped as rings, bio-balls, and oriented modular media have been used in various applications. In some cases, AFs rely on trapping microbial solids within the media rather than using a true biofilm for microbial activity. Thus, the term “fixed-film digesters” should be used to designate true biofilm reactor designs.

In immobilized reactors where a highly degradable, high-COD wastewater (>20 g/liter) is fed, effluent recycling can be employed to overcome localized acidification of the microbial biomass. In addition, highly acidic wastewater can benefit from effluent recycle to minimize the requirement for added alkali by using the alkalinity of the effluent. Phased digestion is often employed for highly degradable waste, where a primary acidogenic reactor is operated at short HRT to form intermediate acids, which are then fed into a methanogenic reactor. This approach can control sharp pH swings, enhance biofilm and granular sludge activity, and lower overall process HRT. A further refinement involves staging, where reactors are employed in series to achieve higher treatment efficiencies. The first reactor is optimized to maximize biogas production (higher OLR), whereas the second reactor is optimized for treatment efficiency (lower OLR).

INOCULATION

The use of a source high in anaerobic microbes (e.g., digester effluent) to start up an anaerobic system is called inoculation. The quality and quantity of inoculum are critical to the performance, time required, and stability of biomethanogenesis during commissioning (start-up) or restart of an anaerobic digester. Much agricultural processing occurs on a seasonal basis, and at the start of a new campaign, the anaerobic treatment operation must be restarted after a period of being idled. In addition, a digester may need inoculation after maintenance operations. In manures and some wastes, the microbes needed for digestion may be already present in the waste in small numbers, albeit sufficient to act as an inoculum, and will develop into a fully functional bacterial population if the right conditions are provided, including a suitable temperature and retention time. Other wastes, especially from industry, may be relatively sterile and require the addition of inoculum. With batch and plug flow designs, inoculum must be added with the feed and low inoculum levels may lead to imbalance due to the more rapid growth rate of acid-forming bacteria (compared to methanogens) and depression of pH. Depending on the buffering capacity (alkalinity), a digester may be able to overcome low inoculum rates.

Granular sludge, the microbial by-product from UASB reactors, has been shown to be a practical source for inoculum due to its stability in storage, microbial density, and availability. Granular sludge may be used to enhance methanogen populations for start-up of complete-mix reactors and anaerobic filters as well as UASBs. Start-up of immobilized systems requires that biofilm or granule growth be optimized to achieve design performance quickly. During start-up, performance parameters (methane gas content, ratio of acids-to-alkalinity, and pH) should be carefully monitored to ensure that performance is not deteriorating. In many applications, a high inoculation rate is not feasible or digester effluent is not available. Under such circumstances, one must obtain inoculum from an anaerobic environment (anaerobic sediments or animal manure) and gradually develop and acclimate the inoculum to the level needed. The major obstacle to overcome is the fact that, during growth toward a mature population, acid formers may grow faster than methanogens, leading to an increase in volatile organic acids, reduced pH, and loss of methane production. This can be prevented by buffering the system and/or reducing the feed loading rate.

NUTRITION

Nitrogen and phosphorus are the major nutrients required for anaerobic digestion. These elements are building blocks for cell synthesis, and their requirements are directly related to the microbial growth in anaerobic digesters. An empirical formula for a typical anaerobic bacterium is $C_5H_7O_2NP_{0.06}$ (Speece, 1996). Thus, the nitrogen and phosphorus requirements for cell growth are 12 and 2%, respectively, of the volatile solids converted to cell biomass. If 10% of the degradable solids are converted into microbial biomass, this would be equivalent to a requirement of 1.2 and 0.2% of the biodegradable volatile solids, respectively, for nitrogen and phosphorus. Ammonia is also an important contributor to the buffering capacity in digesters but can be toxic to the process at high levels.

Methane production and volatile acid utilization may be enhanced when micronutrients are added to nutrient-deficient substrates. Requirements for several micronutrients have been identified, including iron, copper, manganese, zinc, molybdenum, nickel, and vanadium (Wilkie et al., 1986; Speece, 1996). Available forms of these nutrients may be limiting because of their ease of precipitation and removal by reactions with phosphate and sulfide. Limitations of these micronutrients have been demonstrated in reactors in which the analytical procedures failed to distinguish between available and sequestered forms. Other nutrients needed in intermediate concentrations include sodium, potassium, calcium, magnesium, and sulfur. Combining wastes is an effective means of overcoming nutrient limitations. Codigestion with manure often enhances the conversion of other biomass and waste feedstocks through balancing micronutrients.

CONTROL/TOXICITY

Biological methanogenesis has been reported at temperatures ranging from 2°C (in marine sediments) to over 100°C (in geothermal areas). Most applications of this fermentation have been performed under ambient (15 to 25°C), mesophilic (30 to 40°C), or thermophilic (50 to 60°C) temperatures. In general, the overall process kinetics doubles for every 10-degree increase in operating temperature, up to some critical temperature (about 60°C) above which a rapid drop-off in microbial activity occurs. Most commercial anaerobic digesters are operated at mesophilic or ambient temperatures. A higher operating temperature permits reduced reactor size.

Thermophilic digesters exhibit some differences compared to mesophilic digesters. The microbial populations operating in the thermophilic range are genetically unique, do not survive well at lower temperatures, and can be more sensitive to temperature fluctuations outside their optimum range. Also, ammonia is more toxic in thermophilic digesters due to a higher proportion of free ammonia. Although thermophilic digesters have higher energy requirements, heat losses can be minimized through effective insulation and use of heat exchangers to reduce effluent heat losses. Thermophilic operation is practiced when the reduced reactor size justifies the higher energy requirements and added effort to ensure stable performance, when process wastewater is already hot, or when pathogen removal is of greater concern.

Biomethanogenesis is sensitive to several groups of inhibitors including alternate electron acceptors (oxygen, nitrate, and sulfate), sulfides, heavy metals, halogenated hydrocarbons, volatile organic acids, ammonia, and cations. The intermittent presence of microbial inhibitors in the wastewater stream can lead to serious process upsets and failure. The toxic effect of an inhibitory compound depends on its concentration and the ability of the bacteria to acclimate to its effects. The inhibitory concentration depends on different variables, including pH, HRT, temperature, and the ratio of the toxic substance concentration to the bacterial mass concentration. Antagonistic and synergistic effects are also common. Methanogenic populations are usually influenced by dramatic changes in their environment but can be acclimated to otherwise toxic concentrations of many compounds.

Organic acids, pH, and alkalinity are related parameters that influence digester performance. Under conditions of overloading and the presence of inhibitors, methanogenic activity cannot remove hydrogen and organic acids as fast as they are produced. The result is accumulation of acids, depletion of buffer, and depression of pH. If uncorrected via pH control and reduction in feeding, pH will drop to levels that stop the fermentation. Independent of pH, extremely high volatile acid levels (>10,000 mg/liter) also inhibit performance. The major alkalis contributing to alkalinity are ammonia and bicarbonate. The most common chemicals for pH control are sodium hydroxide, lime, magnesium hydroxide, and sodium bicarbonate. Lime produces calcium bicarbonate up to the point of solubility of 1,000 mg/liter. Sodium bicarbonate adds directly to the bicarbonate alkalinity without reacting with carbon dioxide. However, precautions must be taken not to add this chemical to a level of sodium toxicity (>3,500 mg/liter). Currently, the control of feed rate to an anaerobic digester most often relies on off-line measurements of volatile organic acids to prevent process upset through manual intervention. Several investigators have advocated control schemes based on biogas production rate, alkalinity, liquid-phase hydrogen, pH, and digester substrate concentration.

BIOGAS USE

Biogas is a flexible form of renewable energy that may be used directly for process heat and steam or converted to electricity in reciprocating engines, gas turbines, or fuel cells. Biogas is composed mostly of methane, as is natural gas, but may contain some impurities such as hydrogen sulfide. Biogas can be used readily in all applications designed for natural gas such as direct combustion for absorption heating and cooling, cooking, space and water heating, and drying. Biogas can also be upgraded to natural gas specifications and injected into the existing network of natural gas pipelines. Biogas may also be catalytically transformed into hydrogen, ethanol, or methanol.

If cogeneration is employed in the biogas conversion system, heat normally wasted may be recovered and used for hot water production. In gas turbines, the waste heat may be used to make steam and drive an additional steam turbine, with the final waste heat going to hot water production. This is termed a combined cycle cogeneration system. Combining hot water recovery with electricity generation, biogas can provide an overall conversion efficiency of 65 to 85%.

For smaller biogas installations, shaft horsepower and electrical generation are most effectively achieved by the use of a stationary internal combustion engine. Adequate removal of hydrogen sulfide is important to reduce engine maintenance requirements. If compressed for use as an alternative transportation fuel in light and heavy-duty vehicles, biogas can use the same existing technique for fueling as currently used for compressed-natural-gas vehicles. In many countries, biogas is viewed as an environmentally attractive alternative to diesel and gasoline for operating buses and other local transit vehicles. The exhaust fume emissions from methane-powered engines are lower than the emissions from diesel and gasoline engines. Also, the sound level generated by methane-powered engines is generally lower than that generated by diesel engines.

WASTE RESOURCES

Recently, anaerobic wastewater pretreatment has attained extensive acceptance for a variety of industrial wastewaters associated with food processing, beverages, breweries, distilleries, and most recently pulp and paper production. Batch operation of the production sequence is common in these industries, producing a wastewater of variable strength and quantity, complicating the operation of a continuous biological treatment system. A few examples of agricultural and industrial waste streams are identified in Table 2. Traditionally, treatment of manures and municipal sludge have been the most prominent applications of anaerobic digestion, and there is currently a resurgence in the promotion of on-farm biogas production from animal manure (see the Agstar Program, U.S. Environmental Protection Agency; http://www.epa.gov/agstar/). Anaerobic digestion of municipal sludge is applied at many municipal wastewater treatment plants. However, the pretreat-

Table 2. Examples of agricultural and industrial wastewater strength

Feed source	Wastewater COD (mg/liter)
Beef processing	7,500
Beverage	1,600
Brewery	1,900–2,400
Clam	3,500
Confectionery	9,500
Dairy	1,900–5,260
Distillery	95,000
Ice cream	29,063
Municipal	200
Pharmaceutical	9,985
Pork processing	1,572
Potato	2,000–10,500
Pulp and paper	1,600–16,400
Rendering	8,800
Sauerkraut	10,000
Starch	8,800–11,400
Sugar beet refining	5,000–20,000
Vegetable	2,300–10,000
Whey	8,900
Yeast	30,000

ment of municipal wastewater by high-rate anaerobic treatment offers a new application of biogas production in municipal wastewater treatment works (van Haandel and Lettinga, 1994). Conversion of soluble biochemical oxygen demand in municipal wastewater to biogas avoids much of the costs of aeration and the production of residual sludge requiring disposal.

The organic fraction of municipal solid wastes (MSW) also has a high potential for biogas production. A majority of MSW is disposed of in landfills, many of which are implementing biogas recovery systems. However, nutrients contained in MSW are sequestered in landfills and the land area for these operations is often not suitable for economic development. Separation of the organic fraction of MSW and conversion to biogas can produce compost residuals that are suitable for crop production, which results in a sustainable solid-waste recycling system.

CODIGESTION

Digestion of a given waste can often benefit from codigestion with other waste streams that are locally available. There are many reasons for considering codigestion, including the potential to reach a more favorable economy of scale due to materials handling or optimal production and utilization of biogas. Codigestion may provide increased revenues from tipping fees as well as from enhanced biogas production. Very dry feedstocks may be blended with wastewaters to facilitate handling and digestion. Waste high in protein, which could suffer from ammonia toxicity, can be blended with lignocellulosic materials, which are low in nitrogen, to improve digestion rates. Household or other waste streams can be blended with manure to improve the microbial diversity and contribute essential micronutrients. The organic fraction of MSW is suitable for codigestion with farm and industrial wastes, and many successful examples can be found in Europe (see the European Anaerobic Digestion Network; http://www.adnett.org/). Conversion of agricultural, municipal, and industrial wastes to biogas offers a sustainable means for biofuels production, yet the role of biogas production in the production of other biofuels (e.g., alcohols, biodiesel, hydrogen, and syngas) is also an application worthy of exploitation.

METHANE IN BIOETHANOL PRODUCTION

The production of biomethane at bioethanol production facilities can contribute to the energy requirements of ethanol production or to increasing the energy yields from substrates for sale to local markets as fuel or electricity. Depending on the feedstock and process design, ethanol production results in several by-products (Fig. 2) which may include crop residues, stillage, evaporator condensate, condensed solubles, spent cake and/or distillers' grains, all of which have a high potential for methane production (Table 3). Stillage, a residual of the distillation of ethanol from fermentation liquor, contains a high level of biodegradable COD as well as nutrients and has a high pollution potential (Wilkie et al., 2000). Up to 20 liters of stillage may be generated for each liter of ethanol produced. Conversion of stillage to biogas and application of effluent to croplands results in a more sustainable ethanol production system.

Many ethanol plants minimize effluent discharges by evaporation of the stillage to produce evaporator condensate (used partially for makeup water) and condensed solubles. The evaporator condensate contains volatile fermentation products that can inhibit ethanol fermentation. Anaerobic digestion can remove these fermentation products and provide a liquid more suitable for process recycling. The distillers' grains and condensed solubles are normally blended for use in animal feed as dried distillers' grains and solubles. However, the current rapid expansion of ethanol production could lead to saturation of the feed market with dried distillers' grains and solubles, affecting the sale value of this by-product. Thus, there is an opportunity for biogas production from these by-products to offset facility energy requirements. In cellulosic ethanol production, nonfermentable hydrolysis products can also be converted to methane. Finally, crop residues may also be harnessed for biogas production, which can greatly improve the energy yield from ethanol production.

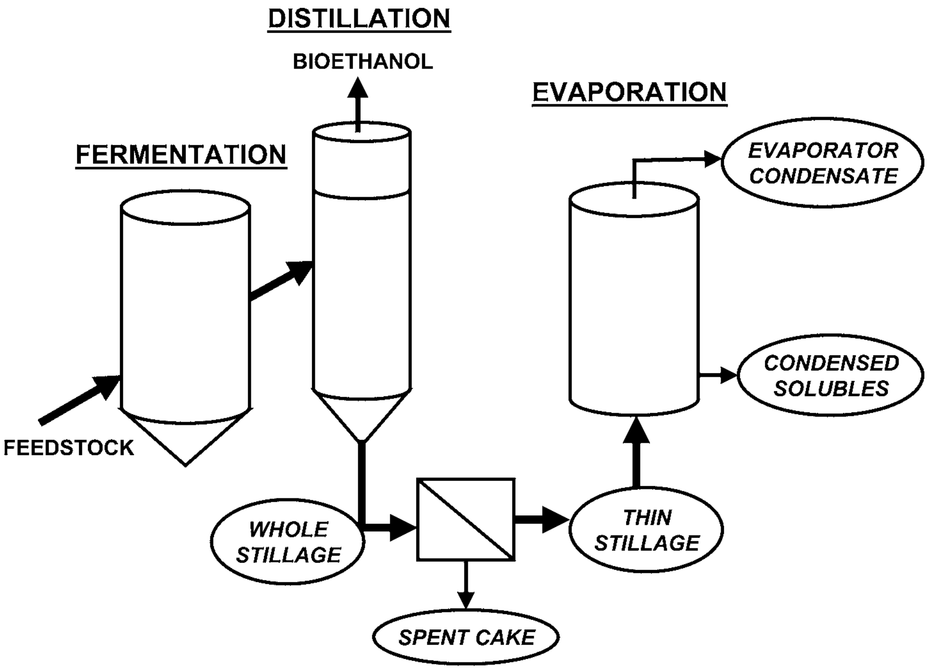

Figure 2. Potential biogas feedstocks from bioethanol production.

METHANE IN BIODIESEL PRODUCTION

Biodiesel is normally produced from either virgin plant oils or waste vegetable oils through a catalytic transesterification process. The typical biodiesel production process uses an alkaline hydrolysis reaction to convert vegetable oil into biodiesel by using methanol, potassium hydroxide, and heat. A transesterification reaction splits the glycerol group from the triglyceride oils, producing methyl esters (biodiesel) and glycerol by-product (Fig. 3). To purify the biodiesel, a washing process is employed to remove soaps, free fatty acids, and excess methanol, producing a washwater by-product. While process yields and inputs depend largely on oil type and quality, for every 100 liters of oil, approximately 25 liters of methanol and 0.8 kg of KOH/NaOH are consumed, yielding around 75 liters of biodiesel and 25 liters of crude glycerol. The washing process produces another 30 liters of biodiesel washwater. Both the crude glycerol and the biodiesel washwater have significant methane production potential. When vegetable oil is pressed from seeds (or algae), there is also a press cake by-product along with crop residues from harvesting that are both amenable to biogas production (Table 3). Conversion of biodiesel by-products to methane offers a sustainable treatment solution, while also providing additional energy. Methane can also be converted to methanol, an ingredient used in biodiesel production. Also, digester effluent could be used to grow oleaginous algae for biodiesel production.

Table 3. COD of some bioenergy by-products

Feedstock	COD (g/kg)
Ethanol thin stillage from corn	56.0–64.5
Ethanol stillage from beet molasses	55.5–116.0
Ethanol stillage from cane juice	22.0–45.0
Ethanol stillage from cane molasses	22.5–118.0
Ethanol stillage from cellulosics	19.1–140.0
Evaporator condensate	2.6–5.7
Condensed solubles	724
Dried distillers' grains	368
Crude glycerol from biodiesel production	1,800–2,600
Washwater from biodiesel	40.1–161.0
Press cake from oil crops	1,570

METHANE IN THE HYDROGEN ECONOMY

Hydrogen is often considered as a long-term solution to dwindling petroleum supplies and the environmental consequences of petroleum use in the transportation sector. However, hydrogen production and storage are still very expensive. Since water is the primary product of H_2 combustion, the fuel is viewed as a means to eliminate CO_2 emissions. Yet, if H_2 production is from fossil sources, it will still result in significant CO_2 emissions. Only the production of H_2 from renewable energy sources can result in reduced greenhouse gas emissions. One means of renewable H_2 production is through fermentation of organic matter.

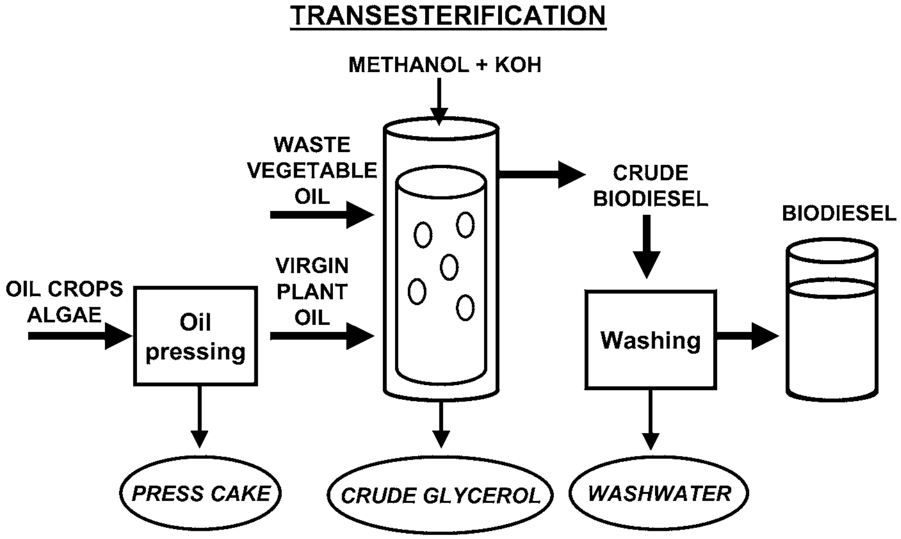

Figure 3. Potential biogas feedstocks from biodiesel production.

However, theoretically, only 33% of the energy in carbohydrates is available for microbial H_2 production due to the requirement to regenerate metabolic reducing potential (Angenent et al., 2004; Hungate, 1974). This means that 66% of the carbohydrate feedstock remains in the fermentation effluent and requires further processing. Anaerobic digestion can easily convert this residual carbon to biomethane, and the methane could then be converted to hydrogen catalytically. Still, the efficiency of conversion for methane production suggests that it is easier to convert all of the carbohydrate directly to methane rather than suffer the low yields of microbial hydrogen production. This methane could be upgraded to natural gas or converted into electricity, both of which are easier to transport than H_2.

There are other means by which methane factors into the hydrogen economy. First, the energy density of H_2 is four times less than that of CH_4 on a molar or volume basis, suggesting that methane could serve as a more efficient storage vector for hydrogen. Secondly, there is an existing infrastructure of pipelines for transporting CH_4 that are not suitable for moving H_2. Capitalizing on this network of pipelines, methane could be transported to regions of demand and converted to H_2 locally as required. Renewable methane, therefore, is an appropriate energy vector even if hydrogen is a desirable replacement fuel.

SYNTHESIS GAS

Another renewable fuel source that could integrate with methane production is the production of synthesis gas (syngas) through thermochemical gasification of biomass. Wastes and biomass crops can be gasified in a reduced atmosphere combustion process to convert the biomass into a mixture of CH_4, CO_2, CO, and H_2. While catalytic conversion of syngas to methanol has historical application for producing “wood alcohol,” the H_2, CO_2, and CO in syngas can be used as a feedstock in methane production. Currently, catalysts for conversion of syngas to mixed higher alcohols (ethanol, propanol, and butanol) are in development, but in any of the catalytic processes, H_2S is problematic for catalyst longevity. Anaerobic digestion could serve as a process for syngas cleanup to convert the mixture to CH_4 (Sipma et al., 2006) and allow more-efficient catalytic conversion to further products ($H_{2,}$ ethanol, or methanol). Pure-culture fermentation of syngas to ethanol is also in development (Younesi et al., 2005), a process which also generates acetate that may in turn be converted to CH_4 via anaerobic digestion.

ENERGY CROPS

Meeting the demand for alternative fuels from seasonal crops grown for bioenergy is potentially tenuous. Storage of crops can result in losses of carbohydrates available for fermentation to ethanol. Direct methane production from energy crops can overcome these losses because of the ability of the anaerobic digestion process to use fermentation intermediates as substrates. Harvested crops can be ensiled to preserve overall energy content, using technology with which farmers are already familiar. Further, any improvement in conversion efficiency that enhances cellulosic ethanol yields is equally applicable for biomass conversion to methane.

Sugarcane, a power crop, has a long growing season in tropical and subtropical climates, and because it is a C4 plant, sugarcane is one of the best plants for collecting and harvesting solar energy. While conversion of the soluble fraction of sugarcane into ethanol has been implemented on a large scale in Brazil, ethanol production facilities are capital intensive, requiring several unit processes and significant energy consumption. However, the soluble fraction of sugarcane can also be converted into biogas. The production of biogas requires much less investment, little energy is consumed in the process, and the potential feedstock is not limited to the sugars but can use the whole sugarcane plant as well as other energy crops. Further, nutrients contained in the cane are conserved in the process and can be returned to the fields to maintain a sustainable production cycle with minimal synthetic fertilizer inputs.

Cane juice can be digested directly to produce methane, without the need for alcohol fermentation, centrifugation and distillation, and the consumption of high-grade energy associated with these processes. Some 47% of the total energy in cane would be present in the biogas produced. The remaining bagasse could still be used for energy production through combustion, as currently implemented in the sugar industry. A further reduction of investment and operational costs and an increase in energy output could be obtained by subjecting not only the juice but the whole cane to anaerobic digestion. Assuming that 70% of the bagasse can be converted into methane, which is a realistic figure for a low-lignin (only 6.3%) plant such as sugarcane, then the energy conversion efficiency would increase to 80% of the energy content of cane (Chynoweth et al., 1993; Pate et al., 1984; van Haandel, 2005). By comparison, only 40% of the energy content of cane is actually converted into alcohol, consuming 24% of the cane energy in the process, while 12% is discharged as wastewater (stillage) and 24% remains in the excess bagasse (van Haandel, 2005).

Corn has also undergone whole-plant conversion to methane. Methane yields for corn at varying harvest times have ranged from 268 to 366 liters/kg of VS (Amon et al., 2007). Table 4 gives ranges of methane yield for various terrestrial and marine energy crops. Methane yields from seaweeds, grasses, and crops all approach theoretical yields, such that as much as 80% of biomass energy content could be recovered in methane.

Table 4. Ranges of biochemical methane potential yield for biomass energy crops[a]

Sample	Methane yield (at STP[b]) (liter/g of VS)
Kelp (*Macrocystis*)	0.39–0.41
Sorghum	0.26–0.39
Sargassum	0.26–0.38
Napiergrass	0.19–0.34
Poplar	0.23–0.32
Water hyacinth	0.19–0.32
Sugarcane	0.23–0.30
Willow	0.13–0.30
Laminaria	0.26–0.28
Municipal solid waste	0.20–0.22
Avicel cellulose	0.37

[a] Modified from Chynoweth et al., 1993.
[b] STP, standard temperature and pressure.

SUMMARY

Biogas production from agricultural, municipal, and industrial wastes is a sustainable means for producing a useful biofuel that can be used for process heating, electrical production, and vehicular fuel. Biogas can be upgraded and injected into natural gas pipelines, leveraging the existing distribution infrastructure. Liquids, slurries, solid wastes, and gaseous waste can all be processed by anaerobic digestion to form biogas. Several digester designs have been developed to optimize processing of different feedstocks. Digester size can be scaled to match the application, and centralized plants, codigesting a mixture of wastes, can be utilized to achieve economies of scale and improved performance. Methane production can be integrated into biorefineries since by-products from production of bioethanol, biodiesel, biohydrogen, and syngas are also suitable for anaerobic digestion, thus increasing net energy yields and recycling valuable nutrients for crop production. Finally, processing of terrestrial and marine energy crops to biomethane can result in higher energy yields than that of other biofuels. Given the diversity of feedstocks and ease of product recovery, methane from organic wastes and energy crops offers a major sustainable energy solution that is renewable, carbon dioxide neutral, and locally based, thereby protecting the environment, creating jobs, and strengthening local economies.

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