3. Upgrading Dairy Biogas to Biomethane and Other Fuels

Dairy biogas can be combusted to generate electricity and/or heat. This report, however, focuses on alternate uses of biogas including the upgrading of biogas to biomethane, a product equivalent to natural gas or other higher-grade fuels. Biomethane, which typically contains more than 95% CH_4 (with the remainder as CO_2), has no technical barrier to being used interchangeably with natural gas, whether for electrical generation, heating, cooling, pumping, or as a vehicle fuel. The process can be controlled to produce biomethane that meets a pre-determined standard of quality. Biomethane can also be put into the natural gas supply pipeline, though there are major institutional barriers to this alternative.

As discussed in Chapter 2, raw dairy biogas typically contains 55% to 70% CH_4 and 30% to 45% CO_2 along with other impurities such as H_2S and water vapor. To produce biomethane from biogas, the H_2S, moisture, and CO_2 must be removed. This chapter provides an overview of the types of processes that can be used to remove these components, reviews the associated environmental impacts, and suggests the most practical processes for small facilities typical of dairy farm applications. In addition, this chapter explores the possibility of upgrading biogas to produce various higher-grade fuels:

- Compressed biomethane (CBM), which is equivalent to compressed natural gas (CNG)
- Liquid-hydrocarbon replacements for gasoline and diesel fuels (created using the Fischer-Tropsch process)
- Methanol
- Hydrogen
- Liquefied biomethane (LBM), which is equivalent to liquefied natural gas (LNG)

Upgrading Biogas to Biomethane

Biogas upgrading, or "sweetening," is a process whereby most of the CO_2, water, H_2S, and other impurities are removed from raw biogas. Because of its highly corrosive nature and unpleasant odor, H_2S is typically removed first, even though some technologies allow for concurrent removal of H_2S and CO_2. The following sections discuss various removal technologies with specific emphasis on those technologies most suitable for on-farm use.

Technologies for Removal of Hydrogen Sulfide from Biogas

The concentration of H_2S in biogas generated from animal manure typically ranges between 1,000 to 2,400 ppm, depending in large part on the sulfate content of the local water. Minor quantities of mercaptans (organic sulfides) are also produced, but are removed along with H_2S and need not be addressed separately. Even in low concentrations, H_2S can cause serious

corrosion in gas pipelines and biogas conversion and utilization equipment as well as result in unpleasant odors and damage to the metal siding and roofing of buildings (Mears, 2001).

H_2S can be removed by a variety of processes, each of which is described below:

- Air injected into the digester biogas holder
- Iron chloride added to the digester influent
- Reaction with iron oxide or hydroxide (iron sponge)
- Use of activated-carbon sieve
- Water scrubbing
- Sodium hydroxide or lime scrubbing
- Biological removal on a filter bed

Air/Oxygen Injection

When air is injected into the biogas that collects on the surface of the digester, thiobacilli bacteria oxidize sulfides contained in the biogas, reducing H_2S concentrations by as much as 95% (to less than 50 ppm). The injection ratio is typically a 2% to 6% air to biogas ratio (a slight excess of O_2 over the stoichiometric requirement). Thiobacilli bacteria naturally grow on the surface of the digestate, and do not require inoculation. The by-product of this process is hydrogen and yellow clusters of elemental sulfur on the surface of the digestate.

Air injection directly into the digester's gas holder, or, alternatively, into a secondary tank or biofilter is likely the least expensive and most easily maintainable form of scrubbing for on-farm use where no further upgrading of biogas is required (i.e., when the biogas is being cleaned solely to prevent corrosion and odor problems, not to increase its methane content). However, the addition of the proper proportion of air presents significant control problems. Without careful control over the amount of air injected, this process can result in the accidental formation of explosive gas mixtures. Furthermore, such process results in some dilution with nitrogen (N_2), which is undesirable if CO_2 is to be subsequently removed and the resulting biomethane compressed for use as a vehicular fuel. Residual oxygen (O_2) would also be a concern for a pressurized gas.

Iron Chloride Injection

Iron chloride reacts with H_2S to form iron sulfide salt particles. Iron chloride can be injected directly into the digester or into the influent mixing tank. This technique is effective in reducing high H_2S levels, but less effective in maintaining the low and stable H_2S levels needed for vehicular fuel applications.

Iron Oxide or Hydroxide Bed

Hydrogen sulfide reacts endothermically with iron hydroxides or oxides to form iron sulfide. A process often referred to as "iron sponge" makes use of this reaction to remove H_2S from gas. The name comes from the fact that rust-covered steel wool may be used to form the reaction bed. Steel wool, however, has a relatively small surface area, which results in low binding capacity for the sulfide. Because of this, wood chips impregnated with iron oxide have been used as preferred reaction bed material. The iron-oxide impregnated chips have a larger surface-to-volume ratio than steel wool and a lower surface-to-weight ratio due to the low density of wood. Roughly 20 grams of H_2S can be bound per 100 grams of iron-oxide impregnated chips.

Iron oxide or hydroxide can also be bound to the surface of pellets made from red mud (a waste product from aluminum production). These pellets have a higher surface-to-volume ratio than steel wool or impregnated wood chips, though their density is much higher than that of wood chips. At high H_2S concentrations (1,000 to 4,000 ppm), 100 grams of pellets can bind 50 grams of sulfide. However, the pellets are likely to be somewhat more expensive than wood chips.

The optimal temperature range for this reaction is between 77° F and 122° F. The reaction requires water; therefore, the biogas should not be dried prior to this stage. Condensation in the iron sponge bed should be avoided since water can coat or "bind" iron oxide material, somewhat reducing the reactive surface area.

The iron oxide can be regenerated by flowing oxygen (air) over the bed material. Typically, two reaction beds are installed, with one bed undergoing regeneration while the other is operating to remove H_2S from the biogas. One problem with this technology is that the regenerative reaction is highly *exothermic* and can, if air flow and temperature are not carefully controlled, result in self-ignition of the wood chips. Thus some operations, in particular those performed on a small scale or that have low levels of H_2S, elect not to regenerate the iron sponge on-site.

For on-farm applications requiring both H_2S and CO_2 removal and compression of the biomethane gas, the iron sponge technology using iron-impregnated wood chips appears to be the most suitable. One farm digester reported that an iron sponge reduced H_2S to below 1 ppm, quite sufficient for all purposes (Zicari, 2003, page 18).

Activated Carbon Sieve

In pressure-swing adsorption systems, H_2S is removed by activated carbon impregnated with potassium iodide. The H_2S molecule is loosely adsorbed in the carbon sieve; selective adsorption is achieved by applying pressure to the carbon sieve. Typically, four filters are used in tandem, enabling transfer of pressure from one vessel to another as each carbon bed becomes saturated. (The release of pressure allows the contaminants to desorb and release from the carbon sieve.) This process typically adsorbs CO_2 and water vapor in addition to H_2S. To assist in the adsorption of H_2S, air is added to the biogas, which causes the H_2S to convert to elementary sulfur and water.

The sulfur is then adsorbed by the activated carbon. The reaction typically takes place at a pressure of around 100 to 115 pounds per square inch (psi) and a temperature of 122 to 158° F. The carbon bed has an operating life of 4,000 to 8,000 hours, or longer at low H_2S levels. A regenerative process is typically used at H_2S concentrations above 3,000 ppm.

Water Scrubbing

Water scrubbing is a well-established and simple technology that can be used to remove both H_2S and CO_2 from biogas, because both of these gases are more soluble in water than methane is. Likewise, H_2S can be selectively removed by this process because it is more soluble in water than carbon dioxide. However, the H_2S desorbed after contacting can result in fugitive emissions and odor problems. Pre-removal of H_2S (e.g., using iron sponge technology) is a more practical and environmentally friendly approach.

Water scrubbing is described below in more detail as a method to remove carbon dioxide.

Selexol Scrubbing

Selexol™ is a solution of polyethylene glycol that can be used for the simultaneous scrubbing of biogas for CO_2, H_2S and water vapor. However, because elementary sulfur can be formed when Selexol is stripped with air (during regeneration), prior removal of H_2S is preferred. The Selexol technology is described in more detail below as a method to remove CO_2.

Sodium Hydroxide Scrubbing

A solution of sodium hydroxide (NaOH) and water has enhanced scrubbing capabilities for both H_2S and CO_2 removal because the physical absorption capacity of the water is increased by the chemical reaction of the NaOH and the H_2S. The enhanced absorption capacity results in lower volumes of process water and reduced pumping demands. This reaction results in the formation of sodium sulfide and sodium hydrogen sulfide, which are insoluble and non-regenerative. (The NaOH also absorbs CO_2, which could, in principle, be partially regenerated by air stripping; however in practice, the process is not regenerative and is thus prohibitively expensive.)

Biological Filter

A biological filter combines water scrubbing and biological desulfurization. As with water scrubbing, the biogas and the separated digestate meet in a counter-current flow in a filter bed. The biogas is mixed with 4% to 6% air before entry into the filter bed. The filter media offer the required surface area for scrubbing, as well as for the attachment of the desulfurizing (H_2S oxidizing) microorganisms. Although biofiltration is used successfully to remove odors from exiting air at wastewater treatment plants, and suitable media (e.g., straw, etc.) is available on farms, some oxygen would need to be added to the biogas. We are unaware of any instance where biofiltration has been usefully applied to remove H_2S from streams of oxygen-free biogas.

Technologies for Removal of Water Vapor

Because biogas from digesters is normally collected from headspace above a liquid surface or very moist substrate, the gas is usually saturated with water vapor. The amount of saturated water vapor in a gas depends on temperature and pressure. Biogas typically contains 10% water vapor by volume at 110° F, 5% by volume at 90° F, and 1% by volume at 40° F (Weast, 1958). The removal of water vapor (moisture) from biogas reduces corrosion that results when the water vapor condenses within the system. Moisture removal is especially important if the H_2S has not been removed from the biogas because the H_2S and water vapor react to form sulfuric acid (H_2SO_4), which can result in severe corrosion in pipes and other equipment that comes into contact with the biogas. Even if the H_2S has been removed, water vapor can react with CO_2 to form carbonic acid (H_2CO_3), which is also corrosive (pH near 5). When water vapor condenses within a system due to pressure or temperature changes, it can result in clogging of the pipes and other problems as well as corrosion.

A number of techniques can be used to remove condensation from a pipe, including tees, U-pipes, or siphons. The simplest method to remove condensation water is to install horizontal pipe runs with a slope of 1:100. A drip trap or condensate drain can then be located at all low points in the piping to remove condensation. However, this will only remove water vapor that condenses in the piping. The simplest means of removing excess water vapor to dew points that preclude downstream condensate in biogas is through refrigeration. In a refrigerator unit, water vapor condenses on the cooling coils and is then captured in a trap.

The dew point of biogas is close to 35° F. As mentioned, at 90° F the biogas contains 5% water vapor, which has a density of about 0.002 lb/ft^3. At 105° F, the water vapor content doubles to 0.004 lb/ft^3. At this temperature, for example, a thousand cow dairy that produces 2,000 ft^3/h of biogas would yield about 4 lb of condensation water per hour (when all the water vapor is condensed). The latent heat of vaporization of water is 1,000 Btu/lb of water. Therefore, condensation of 5 lb of water will require 5,000 Btu/hour, which is a little less than 0.5 ton of refrigeration.

Refrigerators with capacities of 0.5 to 1 ton are commercially available and easily used on a dairy. Scrubbing of the biogas to remove H_2S prior to refrigeration would significantly lengthen the life of the refrigeration unit. The power needed for this type of refrigeration unit would be modest, less than 2% of the biogas energy content.

Technologies for Removal of Carbon Dioxide

The technologies available for removal of CO_2 from dairy manure biogas are typically used for larger scale applications such as upgrading natural gas from “sour” gas wells, sewage treatment plants, and landfills. Because of the different contaminants, scales, and applications, removal of

CO_2 from dairy manure biogas will differ significantly from these applications and requires a case-by-case analysis.

The following processes can be considered for CO_2 removal from dairy manure biogas. The processes are presented roughly in the order of their current availability for and applicability to dairy biogas upgrading:

- Water scrubbing
- Pressure swing adsorption
- Chemical scrubbing with amines
- Chemical scrubbing with glycols (such as Selexol™)
- Membrane separation
- Cryogenic separation
- Other processes

Water Scrubbing

When water scrubbing is used for CO_2 removal, biogas is pressurized, typically to 150 to 300 pounds per square inch, gauge (psig) with a two-stage compressor, and then introduced into the bottom of a tall vertical column. The raw biogas is introduced at the bottom of the column and flows upward, while fresh water is introduced at the top of the column, flowing downward over a packed bed. The packed bed (typically a high-surface-area plastic media) allows for efficient contact between the water and gas phases in a countercurrent absorption regime. Water often pools at the bottom of the contact column and the biogas first passes through this water layer in the form of bubbles. The CO_2-saturated water is continuously withdrawn from the bottom of the column and the cleaned gas exits from the top.

A purity of about 95% methane can be readily achieved with minimal operator supervision in a single pass column. After scrubbing, the water can be regenerated (i.e., stripped of CO_2 by contacting with air at atmospheric pressures, either in a packed bed column similar to the one used for absorption, or in a passive system such as a stock pond).

This type of system was apparently first used in the USA for stripping CO_2 from biogas at a wastewater treatment plant in Modesto, California and is currently used at the King County South Wastewater Treatment Plant in Renton, Washington (Figure 3-1). It is also the most commonly used biogas clean-up process in Europe. The Modesto plant, operated in the 1970s and early 1980s, was rather simple and crude, and had no separate H_2S removal system. It produced a renewable methane stream that was compressed to fuel vehicles at the sewage treatment plant. The system was discontinued due to corrosion problems as well as lack of interest when the energy crisis abated.

At the Renton plant near Seattle, approximately 150,000 ft^3 of biomethane (95%+ CH_4) are produced daily and injected into a medium-pressure pipeline. Because a large amount of treated water is available at Renton (and other wastewater treatment plants), a single-pass process with no water regeneration stage can be used, which saves the cost of regenerating CO_2-laden water. Dairy operations could similarly avoid the regeneration stage by using available on-farm stock water.

In addition to being a simple, well-established, and relatively inexpensive technology, water scrubbing typically loses relatively little CH_4 (less than 2%) because of the large difference in solubility of CO_2 and CH_4. Methane losses can be larger, however, if the process is not optimized.

A water scrubbing system preceded by H_2S removal would be a practical, low-cost process for upgrading dairy biogas to biomethane. It is important that the H_2S be removed prior to the removal of the CO_2, as H_2S is highly corrosive and would result in decreased life and higher maintenance of the subsequent compressors required in the CO_2-removal step.

Figure 3-1 Carbon dioxide absorption towers at the King County South Wastewater Treatment Plant

Our research indicates that all but one or two of the dozen municipal wastewater treatment plants where sewage biogas is upgraded use water scrubbing. The other main processes used for CO_2 removal at wastewater treatment facilities are pressure swing adsorption (used mainly by Kompogas in Switzerland) and membrane technology, both of which are discussed below. Solvents other than water (e.g., glycols or amines) have not been used except at a few landfill sites and at the Gasslosa plant in Sweden, where the Cirmac process is used (see discussion, below).

One reason for the prevalence of water scrubbing at wastewater treatment plants is that these plants have an abundance of water, and thus can use a single-pass system, with no need for water regeneration. This greatly simplifies operations. Some dairy operations also have water in sufficient quantities for a single-pass system, and could use the wastewater from a water-scrubbing system for certain dairy operations such as washing stalls. If the wastewater were stored in stock ponds, the CO_2 would be released on its own over a period of a few days (faster with some aeration).

The disadvantage of water scrubbing is that it is less efficient than other processes, both in terms of CH_4 loss and energy. However, some of the energy inefficiency of the process may be offset by the use of a single-pass water scrubbing system, since other processes require a regeneration stage.

Water scrubbing is the most applicable CO_2 scrubbing process for use in an agricultural setting because of its simplicity and low cost. On a dairy farm, these factors would be more important than efficiency, reduced footprint, and redundancy. Another advantage of water scrubbing over some other processes is that water is fairly easy to dispose of whereas the chemicals used in some of the other processes may require special handling and disposal when spent.

Pressure Swing Adsorption

This approach uses a column filled with a molecular sieve (typically an activated carbon) for differential sorption of the gases, such that CO_2 and H_2O adsorb preferentially, letting CH_4 pass through. The process is operated under moderate pressures. Several columns, typically four, are operated sequentially to reduce the energy consumption for gas compression (Figure 3-2) and the gas pressure released from one vessel is subsequently used by the others. The first column cleans the raw gas at about 90 psi to an upgraded biogas with a vapor pressure of less than 10 ppm H_2O and a CH_4 content of 96% or more. In the second column, the pressure of 90 psi is first released to approximately 45 psi by pressure communication with the fourth column, which was previously degassed by a slight vacuum. The pressure in the second column is then reduced to atmospheric pressure and the released gas flows back to the digester so that the CH_4 can be recovered. The third column is evacuated from about 15 to about 1 psi. The desorbed gas consists predominantly of CO_2 and is normally vented to the environment even though it contains some

residual CH_4. To reduce CH_4 losses, the system can be designed so that desorbed gases recirculate to the pressure swing adsorption system or even the digester.

This process produces a water-free gas that is cleaner than gas produced by other techniques such as water scrubbing; however, it requires considerably more sophistication and increased process controls, including careful recycling of a fraction of the gas to avoid excessive CH_4 losses. Another drawback is its susceptibility to fouling by contaminants in the biogas stream.

Automated cycling of multiple columns is used by Air Products, Inc. at the Olinda Landfill in California. Smaller automated systems would be more applicable to dairy farm use.

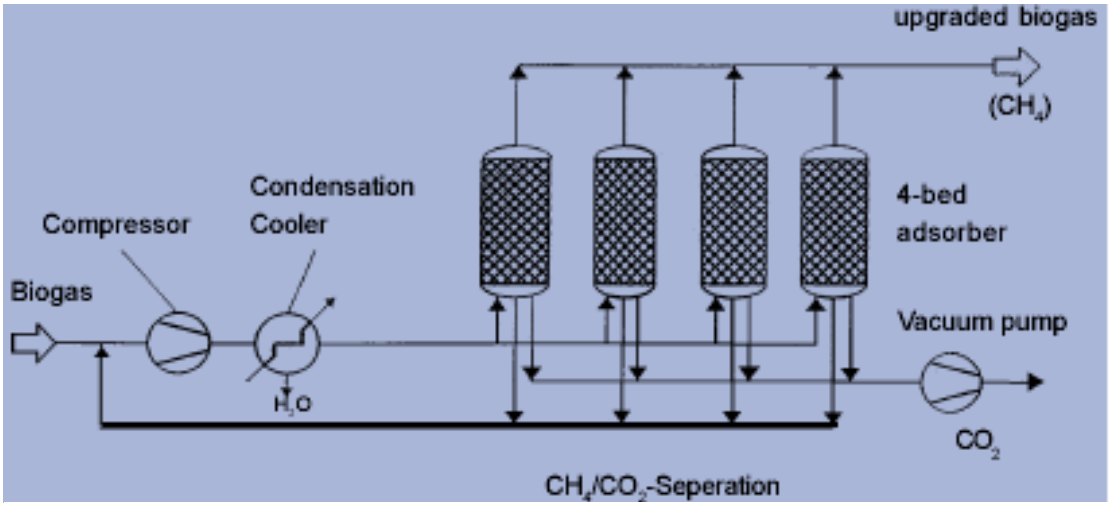

Figure 3-2 Schematic of a pressure swing absorption system with carbon molecular sieves for upgrading biogas

Chemical Scrubbing With Amine Solvents

Amine scrubbing is widely used in food-grade CO_2 production and has also become the preferred technology for large-scale systems that recover CO_2 from natural gas wells. More recently, amine scrubbing technologies have played a key role in CO_2 removal from power plant flue gases as part of GHG abatement programs. The process uses organic amines (monoethanolamine [MEA], diethanolamines [DEA], and diglycolamines [DGA]) as absorbers for CO_2 at only slightly elevated pressures (typically less than 150 psi). The amines are regenerated by heating and pressure reduction to drive off the CO_2, which can be recovered as an essentially pure by-product of the process.

The principle of amine scrubbing is represented by the following general chemical equations:

CO_2 sorption: $RNH_2 + H_2O + CO_2 \rightarrow RNH_3^+ HCO_3^-$ (under pressure) (1)

CO_2 desorption: $RNH_3^+ HCO_3^- \rightarrow RNH_2 + H_2O + CO_2$ (low pressure, some heat) (2)

(R represents the remaining organic component of the molecule that is not relevant to this equation.)

One advantage of the amine approach is the extremely high selectivity for CO_2 and the greatly reduced volume of the process; one to two orders of magnitude more of CO_2 can be dissolved per unit volume using this process than with water scrubbing. If waste heat is available for the amine-scrubbing stage, the overall energy use is lower than for other processes such as Selexol™ or water scrubbing. The process has been scaled-down for landfill applications and works relatively well.

The main problems are corrosion, amine breakdown, and contaminant buildup, which make it problematic to apply this process to small-scale systems such as dairy farms. However, dairy manure biogas typically has fewer contaminants of concern than biogas sources such as landfills, and steel pipes can be used to minimize corrosion.

Cirmac, a Dutch company, has developed a proprietary amine (COOAB™) scrubbing process that is used at the Gasslosa biogas plant in Boras, Sweden (Figure 3-3). One advantage of this process is its very low CH_4 loss; one disadvantage is that it is a more complex technology. However, most of the system complexities are not visible to the operator of the COOAB packaged unit and Cirmac is actively promoting its technology for small-scale biogas upgrading (see <http://www.cirmac.com/>).

Chemical Scrubbing with Polyethlylene Glycols

Polyethylene glycol scrubbing, like water scrubbing, is a physical absorption process. Selexol™ is the main commercial process using this solvent, and it is used extensively in the natural gas industry as well as other applications. Carbon dioxide and H_2S have even greater solubility

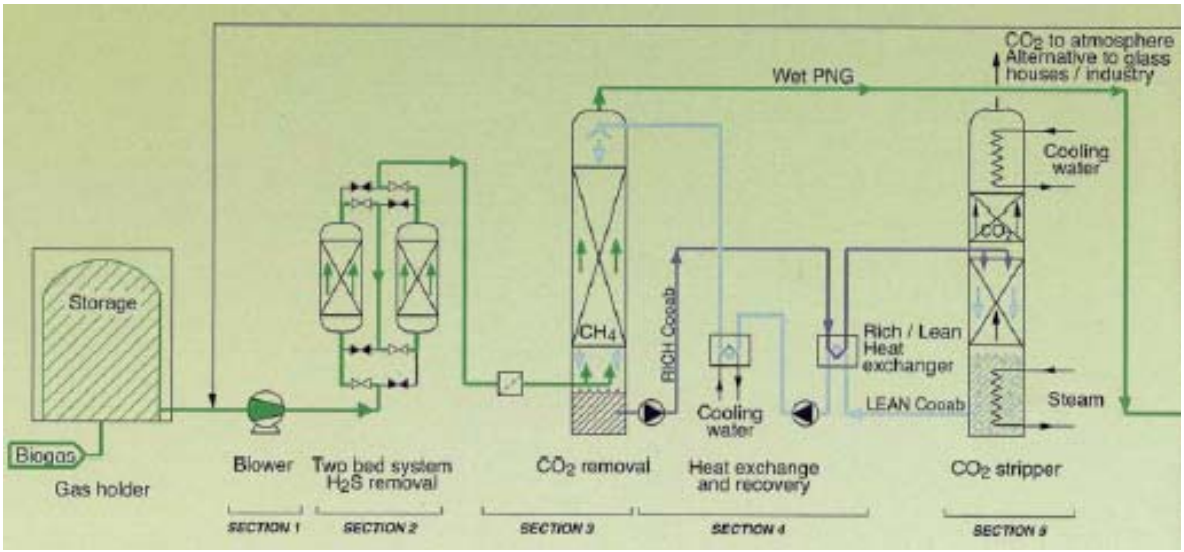

Figure 3-3 Cirmac amine carbon dioxide absorption process (LP Cooab™) for upgrading biogas (Source: Cirmac, Undated)

relative to methane in Selexol fluid than in water, which results in a lower solvent demand and reduced pumping. Selexol is typically kept under pressure, which improves its capability to absorb these contaminants. In addition, water and halogenated hydrocarbons (contaminants in landfill gas) are removed when scrubbing biogas with Selexol.

Selexol scrubbing systems are always designed with recirculation. The Selexol solvent is stripped with steam; stripping the Selexol solvent with air is possible but not recommended because of the formation of elementary sulfur. (Prior removal of H_2S is preferred for this reason.) The Selexol process has been used successfully to upgrade landfill gas at several landfill sites in the USA. The major drawback is that the process is more expensive for small-scale applications than water scrubbing or pressure swing adsorption.

Membrane Separation

The most common membrane separation process uses pressure and a selective membrane, which allows preferential passage of one of the gases. Due to imperfect separation, several stages are generally used. During the 1990s Clean Fuels Corporation designed and operated a landfill gas purification system that produced vehicular fuel at the Puente Hills Landfill in Los Angeles County (Roe, et al., 1998). This small system, which treated only about 1% of the total landfill gas flow, had a capacity of about 90 standard cubic feet per minute (scfm) and produced the natural gas equivalent of about 1,000 gallons of gasoline daily.

The Puente Hills process (shown schematically in Figure 3-4) used a water knockout tank to remove condensate from the raw landfill gas, followed by a three-stage compression system that

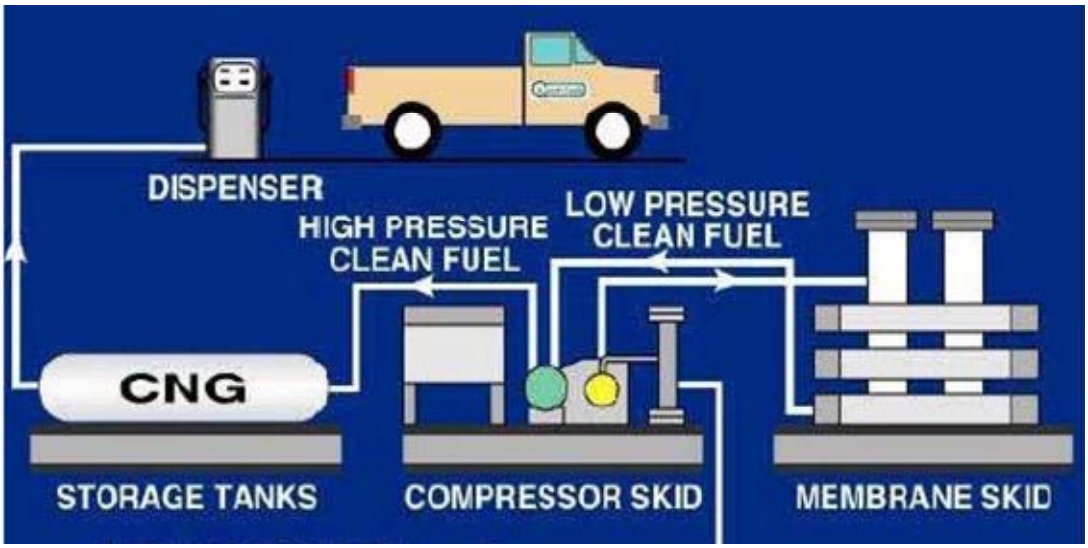

Figure 3-4 Schematic of Puente Hills landfill gas carbon dioxide – methane separation process (Source: Sanitation Districts of Los Angeles County, http://www.lacsd.org/swaste/Facilities/LFGas/CNGFacility.htm)

increased pressure from 41 to 150 to 525 psi. Next, an activated carbon absorption system removed impurities and a heater increased the gas temperature to 140° F before the gas entered a three-stage acetate membrane separation unit. About 15% of the gas, which contained about 80% CH_4, was recycled to the head of the system. The remaining 85% of the gas, which contained about 96% CH_4, was compressed and stored at 3,600 psi. Some tanks were kept at medium and others at higher pressure, allowing for sequential fast filling by the fuel dispenser.

Major problems with compressor oil carryover, corrosion, and other operational issues were encountered at the Puente Hills Landfill. Membrane life was not as long as expected, with a 30% loss in permeability after 1.5 years. The process had to be carefully monitored, in part due to the variable nature of landfill gas, which often contains large amounts of nitrogen gas from air intrusion, in addition to other contaminants. Methane losses were significant, but not documented.

Membrane processes are also used at several plants in Europe, but less detail is available on these operations. New low-pressure membranes are being developed that could be more effective for CO_2 removal.

Cryogenic Separation

Because CO_2, CH_4, and contaminants all liquefy at very different temperature-pressure domains, it is possible to produce CH_4 from biogas by cooling and compressing the biogas to liquefy CO_2 which is then easily separated from the remaining gas. The extracted CO_2 also can be used as a solvent to remove impurities from the gas. A cryogenic separation has been proposed by Acrion Technologies (Cleveland, Ohio) to purify landfill gas, which contains halocarbons, siloxanes and VOCs and is thus more challenging to clean-up than dairy manure biogas. In the Acrion scheme, considerable CO_2 is still present in the biomethane after processing. Removal of this CO_2 requires a follow-up membrane separation step, or CO_2 wash process, mainly to remove impurities and produce some liquid CO_2 (Figure 3-5). This wash process has been demonstrated at a landfill in Columbus, New Jersey.

The economics of cryogenic separation still need to be assessed and further development is needed before cryo-separation can be considered ready for applications. A potential problem with cryo-separation is that its costs of separation tend to drop sharply with increasing scale and its cost-effectiveness at small scales has not been established. No information is available on using cryogenic separation solely for CH_4 purification (i.e., not in conjunction with other cleanup technologies).

This process might be worth considering if the end objective is to produce liquefied biomethane (LBM), a product equivalent to liquefied natural gas (LNG). In this case, the refrigeration process needed for cryo-separation would likely be synergistic with the further cooling required for LBM production. Determining the actual technical and economic feasibility of combining these processes, however, is beyond the scope of this study.

Other Technologies for Carbon Dioxide Removal

There are literally dozens of vendors of alternative technologies for CO_2 removal from gases. Many of these have been spurred by recent interest in separation of CO_2 from power plant flue gases for purposes of CO_2 sequestration. Commercial CO_2 removal technologies have been in use for several decades to produce CO_2 for processed foods (e.g., soft drinks, etc.), for tertiary oil recovery, and for natural gas purification. It is not apparent, however, that the present increase in research in this field has produced any new or superior technologies applicable to biogas upgrading. The main commercial processes for power plant flue gas clean-up are the amine processes (described above), which have proved to have superior economic performance. Organic solvents—in particular methanol—have also been used for CO_2 removal, but have also fallen out of favor due to high costs. The use of hot potassium carbonate solutions, which are often mixed with various other chemicals to facilitate the process, are similarly considered obsolete technology. A recently proposed process uses refrigeration to produce CO_2 clathrates (water complexes) that can be easily recovered; however, this process is still at a very early exploratory stage. In conclusion, despite the worldwide search for "game-changing" technologies for CO_2 removal from power plant emissions, none have yet been identified.

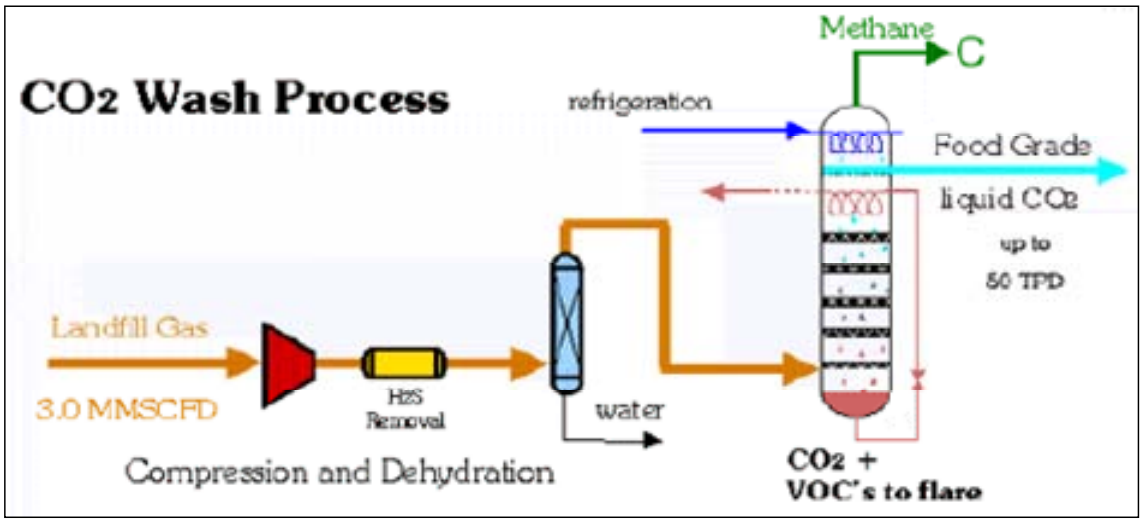

Figure 3-5 Carbon dioxide scrubbing process developed by Acrion Technologies (source: Acrion Co. <www.acrion.com>)

Environmental Effects of Gas Cleanup Technologies

Materials used in adsorption gas cleanup technologies such as iron sponge, activated carbon sieve, and other molecular sieves can be regenerated. The iron sponge bed can be recovered by oxidizing it with air, forming iron oxide and elemental sulfur. Activated carbon is typically regenerated with steam, and other molecular sieves (such as zeolites) are regenerated by passing a heated gas (400^{o} to 600^{o} F) over the bed. The sulfur remains attached to the surface of the iron

sponge bed material after regeneration, requiring replacement of the bed media after a number of cycles. Elemental sulfur is not hazardous, and the bed material can be disposed of through composting or at a landfill (F.Varani, Honeywell PAI, personal communication, September 2004). Thus, these technologies are considered environmentally friendly.

Liquid based (aqueous) absorption processes such as scrubbing with water, sodium hydroxide, amines, or glycols present disposal challenges. The most benign of these solvents is water. However, H_2S should be removed by a method other than water scrubbing to prevent fugitive H_2S emissions

Chemical removal processes have significant potential for chemical pollution from the accidental release of chemicals or from their final disposal. Chemicals may degrade during use because of contamination with pollutants in the biogas (although this should be less of a problem with dairy biogas than with sewage or landfill gas), corrosion, and other problems. The disposal of spent and degraded chemicals may pose a hazardous waste disposal issue for both CO_2 and H_2S scrubbing. The use of sodium hydroxide for H_2S scrubbing results in large volumes of wastewater contaminated with sodium sulfide and sodium hydrogen sulfide, insoluble salts whose disposal is environmentally sensitive. Polyethylene glycol (Selexol process) and amines are not as problematic as these solvents are recirculated and stripped of elemental sulfur using an inert gas or steam.

Biological gas clean-up technologies for H_2S, such as a biological filter bed or injection of air into the digester gas holder, result in the sulfur particles flowing out with the digestate. Due to the low concentrations of H_2S in the dairy biogas and the large volumes of digestate involved this does not result in a disposal problem.

Possible Design for Small Dairy Biomethane Plant

A small dairy biogas upgrading plant might consist of the following:

- Iron sponge unit to remove H_2S
- Compressors and storage units
- Water scrubber with two columns to remove CO_2
- Refrigeration unit to remove water
- Final compressor for producing CBM, if desired

Table 3-1 provides basic system parameters for such a system, which is scaled to a dairy farm with 1,500 cows with an assumed CH_4 production of 30 ft3/cow/day.[1]

Table 3-1 Components for Typical Small Biogas Upgrading Plant

Component	Size/Capacity
Iron sponge H_2S scrubber	• 70,000 ft^3/day • 6 ft. dia x 8 ft. high
First-stage compressor (centrifugal blower)	• intake capacity = 100 ft^3/m compression to 8 psig
Modified piston compressor	• 1st stage compression from 8 to 40 psig • 2nd stage compression from 40 to 200 psig
Pressurized storage tanks	2 x 5,000 gal. propane tanks
Water CO_2 scrubber	• Two 12-inch diameter x 12-ft columns with Jaeger packing • water pump, piping, pressure valves, regulators • operates at pressures between 200 and 300 psig
Flash tank, gas recycler, chiller to reduce moisture	
High-pressure compressor	compression from 200 to 3,000 psig (small unit)
Additional components that may be needed	• refrigeration • contingencies • engineering hook-ups • infrastructure

[1] Various sources provide different average methane yields per cow. For example, Mehta (2002) cites Parsons (1984) as suggesting a biogas yield of 54 ft^3 per cow per day; since biogas has an estimated heat value of 600 Btu/ft^3, this means one cow would generate about 32.4 ft^3/day of CH_4. Other gas yields cited by Mehta (2002) include 139 ft^3/cow/day at Haubenschild Farm (as cited by Nelson and Lamb, 2000) and a design estimate of 65 ft^3/cow/day (Craven Farms, as cited by Oregon Office of Energy). Barker (2001) states that a 1,400 lb cow will yield about 30 ft^3 of CH_4 day. This is also the figure we use in this report based on the following:

1. An average cow weighs 1,400 lb and produces 120 lb/day of manure containing 11.33 lb of volatile solids.
2. Manure is collected within 2 days of deposition.
3. 1 lb of 2-day-old volatile solids from a dairy cow anaerobically digests to produce 3 ft^3 of methane.
4. The percent of manure collected in California, by farm type, is: 90% on flush free stall dairies, 90% of scrape freestall dairies, 60% on flushed feedlane drylot dairies, and 15% on dry lot dairies.
5. Solids separation reduces biogas production potential by 25%.
6. Using flushed and scraped freestall dairies as our standard and multiplying this out: $1.4 \times 11.3 \times 3 \times 0.9 \times 0.75 = 32$ ft^3 of methane per cow, which we have chosen to round conservatively to 30 ft^3/cow for most of our calculations.

The iron sponge H_2S scrubber would be an insulated fiberglass with a removable top cover for spent sponge removal. The iron oxide bed would last about one year. After H_2S removal, compressors would pressurize the gas and two packed columns would be used for the CO_2 water scrubbing process. The total system would be mounted on a small skid including water pump, piping, pressure valves and regulators. Other equipment needed in process would include a flash tank and gas recycler, as well as a chiller to reduce moisture content prior to final compression.

Process water could be re-used on the farm (for dairy barn cleaning, irrigation, or a stock pond). If stored in a stock pond, it could be recycled after a day or two of open air storage.

Figure 3-6 is a schematic of an on-farm water scrubbing process for CO_2 (but does not include iron sponge removal of H_2S). The final stage in the system (also not shown in Figure 3-6) would be a compressor to produce compressed biomethane, assuming this type of vehicle fuel is desired.

Operation and maintenance of this system would be relatively simple, which is one reason it is recommended over other, possibly more efficient, processes. Electricity for the compressors could be produced from an on-site generator using biogas (biogas could also be used to generate power for other on-site uses) or from purchased power. If purchased power were used, the major operating costs for this process would be for power for gas compression.

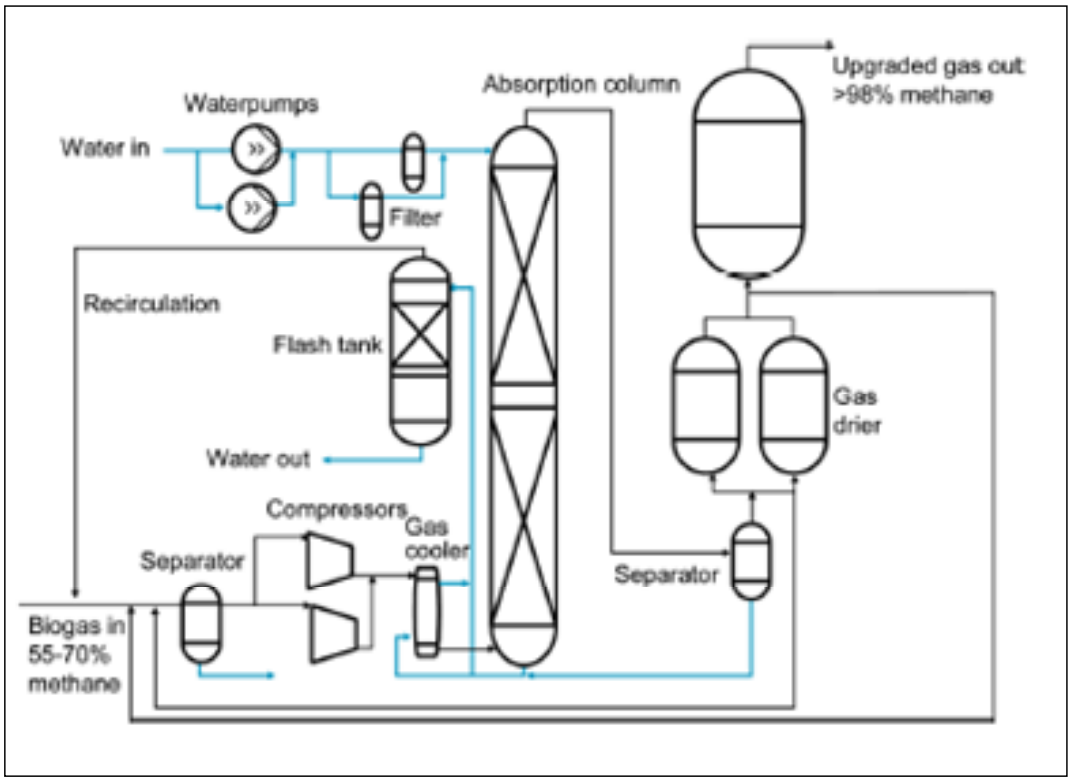

Figure 3-6 Water scrubbing process to remove carbon dioxide from biogas without regeneration (source: Hagen et al., 2001, Figure 7)

Capital and operating costs for a relatively small-scale plant with the capacity to upgrade biogas from 1,500 cows are discussed in more detail in Chapter 8. Our research suggests that a farm of about 1,500 dairy cows is the lower limit of scale for this technology.

Blending Biogas with More Valuable Fuels

The addition of propane or liquefied petroleum gas (LPG), which is gaseous at ambient pressure, is sometimes used to increase the heating value of natural gas in order to meet pipeline quality specifications and could do the same for biomethane. The percentage of propane or LPG mixed in with natural gas tends to be low (i.e., less than 8%) for cost reasons. Since this method does not increase the overall CH_4 content of the gas, it is not by itself sufficient for upgrading biogas to biomethane.

Hypothetically, a small amount of raw or partially purified biogas could be mixed with a larger amount of natural gas from the natural gas pipeline to create a blended feedstock for a town gas system. Although this has been done in Europe, we have no such systems in the USA and blending biogas and natural gas would be inappropriate for producing pipeline quality gas (there would still be too much H_2S and CO_2 present. The basic effect of the addition of the biogas would be to reduce the average CH_4 content of the blended gas feedstock and increase its level of contaminants. As an example, assuming natural gas with 92% CH_4 and raw biogas with 65% CH_4, a blending ratio of 6:1 or greater would yield a blended gas with the required 88% methane or better. Pre-blending of raw or partially purified biogas with natural gas or other fuels offers no advantages in the production of either LNG or CNG.

Compressing Biomethane

Biomethane compressed to about 3,600 psi is referred to in this report as compressed biomethane (CBM). Compositionally, it is equivalent to compressed natural gas (CNG), an alternate vehicular fuel, which contains about 24,000 Btu/gallon compared to approximately 120,000 for gasoline and 140,000 for diesel fuel. Consequently, CNG (or CBM) vehicles have both larger fuel tanks and a more limited driving range than traditionally fueled vehicles. Bi-fueled vehicles that could switch from CNG (or CBM) to gasoline would allow for longer driving ranges and less dependence on CNG refueling stations. However, infrastructure costs for distribution and fueling stations present a major hurdle for off-farm use of dairy biomethane (see Chapter 4).

Converting Biomethane to Non-Cryogenic Liquid Fuels

There is considerable interest in the production of renewable liquid fuels that could be used more directly in the existing transportation fleet and could overcome the volume, range, and weight limitations imposed by CBM (or CNG). For example, the energy contents of methanol and liquefied biomethane (LBM, equivalent to LNG) are about 65,000 and 84,000 Btu/gallon,

respectively, much closer to the energy density of gasoline or diesel fuel than CNG (or CBM) and thus better suited for existing passenger vehicle applications.

In addition to liquefied biomethane (LBM), which is discussed at the end of this chapter, two main technologies exist for converting biogas to liquid fuels: catalytic conversion to methanol, and Fischer Tropsch synthesis for hydrocarbon fuels production. The initial steps to produce these liquid fuels from biomethane—the methane-reforming and catalytic conversion processes—are described below.

Methane-Reforming and Catalytic Conversion Processes

The conversion of methane (from natural gas) to liquid fuels can be accomplished through a methane-reforming process along with steam to produce synthesis gas (consisting of CO, H_2, and $CO_{2)}$. This synthesis gas can then be catalytically converted to methanol or hydrocarbon fuels. The key to these processes is the nature and specificity of the catalysts, as well as the methane to CO-H_2 conversion reaction. The two basic processes used for methane conversion are steam reforming (Equation 3) or dry reforming (Equation 4):

$CH_4 + H_2O \rightarrow CO + 3H_2$	steam reforming, at 1500^o F	(3)
$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	dry reforming, at 2200^o F	(4)
$CO + 2H_2 \rightarrow CH_3OH$	methanol synthesis	(5)
$CO + 2H_2 \rightarrow (CH_2) + H_2O$	Fischer Tropsch	(6)

A range of iron or copper catalysts are typically used for the catalytic conversion process to liquid fuels; different catalysts will selectively produce one product or the other. Furthermore, these catalysts are very sensitive to impurities, specifically H_2S. This requires careful scrubbing of the H_2S, but also of mercaptans (organic sulfur compounds) and other impurities.

The main drawbacks of both methane-reforming and catalytic conversion processes are the high temperatures and pressures at which they must be operated, as well as their complexity. Complexity comes from, among other causes, the requirement for efficient heat (energy) exchange and recovery among process components. Process control is a significant issue. An additional major factor for the poor economies of scale (both capital and operating) of such systems is the requirement for high-pressure compressors. Both processes require a relatively large scale for economic performance as smaller systems are not much cheaper than larger ones.

Biomethane to Gasoline Using the Fischer-Tropsch Process

The Fischer-Tropsch method has been in use since the 1920s to convert coal, natural gas, and other “low-value” fossil fuel products into a high-quality, clean-burning fuel. The performance of Fischer-Tropsch fuels is similar to other fuels such as gasoline and diesel. The drawback of these

fuels is that they are very expensive to produce, even at very large scales. For example, the Fischer-Tropsch process is presently being developed commercially in Qatar, where a 34,000-barrels-per-day plant is being built to convert natural gas to gasoline using the Fischer-Tropsch process, at an investment of about $100/barrel output-year. Two-thirds of this cost is said to be tied to the methane-reforming process, with only one-third tied to the Fischer-Tropsch reaction itself. This cost does not reflect the cost of the infrastructure for getting the gas to the plant, cleaning it up, or getting the product to market.

One major problem is that the Fischer-Tropsch catalysts are far from perfect (the reaction is not sufficiently selective) and the by-products formed—in particular heavier oils and waxes—require further refining to generate a clean, high-value liquid fuel equivalent to gasoline. The by-product fuel would be best used for small-scale applications such as heating or bunker oil, as upgrading of this fuel for other uses would be costly (Dale Simbeck, SFA Pacific, personal communication, 8 November 2004).

Overall, the large economies of scale required for these processes makes them inapplicable to dairy biogas. Another problem is that parasitic energy requirements cause thermal efficiency (fuel energy out/biogas energy fed) to be lower than for other products such as liquefied natural gas.

More fundamentally, for the Fischer-Tropsch process as well as for methanol production, the optimal process is to react the natural gas with both pure O_2 and steam to get a H_2:CO ratio of 1:2.1 (this is slightly higher than the stoichiometry shown above, to account for hydrocarbon molecule and extra hydrogen). Again, such a process is not applicable for dairy-scale operations due to the high cost of O_2 at such scales. Also the high purity of gas required is an issue for small-scale operations.

The project in Qatar demonstrates that the technology is indeed commercial (even with the almost 50% lower oil prices that prevailed at the time of this investment), but it also points to the need for very large investments to achieve economics of scale. If Fischer-Tropsch technologies were economically viable at a small scale, it is likely they would be marshaled for greater use under the current market conditions of nearly $50/barrel of oil. For example, there is considerable interest in capturing the enormous potential of natural gas that is now being flared worldwide, but the Fischer-Tropsch process has not been attempted for this, to our knowledge. The lack of application of Fischer-Tropsch technologies to these natural gas wells suggests that this technology is not yet suitable for small biogas applications.

Biomethane to Methanol

The conversion of methane to methanol is very similar to, but somewhat easier than, the Fischer-Tropsch process, both in terms of engineering and economic principles and application. An advantage of methanol production is that unwanted by-products are minor compared to Fischer-Tropsch, and the fuel obtained is uniform and more easily recovered and produced. The drawback

is that this fuel has very limited demand, particularly now with the phaseout of methyl-tertiary butyl ether (MTBE), a fuel additive introduced in the late 1970s. There are industrial uses for methanol. A potentially expanding market for renewable methanol (biomethanol) is in the production of biodiesel.

A large potential source of biomethanol is from biomass gasification followed by catalytic conversion. Biomass gasification to produce methanol was proposed in the USA during the 1980s and again in the 1990s, when MTBE became an important oxygenated fuel additive. At that time, methanol, an important input to the production of MTBE, sharply increased in price. This economic incentive led several groups to explore the potential of methanol from biogas (see Appendix C for more in-depth discussion of past and present proposed biomethanol projects). Nevertheless, during the past 20 years, no market has developed for methanol as a neat fuel or fuel additive. Methanol has only half the energy content of gasoline; it has a lower vapor pressure than gasoline, it can attack fuel and engine components; and it is toxic. Although these obstacles could be overcome, together with the lack of a methanol vehicle fueling infrastructure, they severely limit the potential of this fuel.

Biogas or Biomethane to Hydrogen Fuel

Perhaps no single fuel has as much promise and presents as many challenging problems as hydrogen. Not surprisingly, there is great interest in the conversion of biogas to hydrogen. However, the only avenue to hydrogen from methane is through the previously discussed gasification/reform and shift reactions, in which CO and H_2 are produced from CH_4, and the CO along with H_2O is converted to H_2 and CO_2. Converting CH_4 to H_2 is not a major challenge, technically, and might even be feasible on somewhat modest scales. Several companies claim to have small-scale methane reformers that can accomplish this, but nothing has yet materialized. (However, Exxon-Mobil is expected to announce a new reformer for on-board conversion of fuels to H_2 in the near future.)

Once H_2 is produced, it could be used for fuel cells in cars or for stationary applications. The latter, however, are of limited interest for small-scale conversion facilities (and electricity can be produced from biogas without the highly expensive and overall inefficient routing through H_2 and then fuel cells).

One critical issue is the high degree of clean-up required before H_2 can be used in fuel cells. The very high purity of H_2 required makes applications to small-scale biogas operations problematic. Although iron sponge and other H_2S removal systems can be highly effective, even occasional breakthroughs or accidents would be catastrophic for fuel cell applications.

Carbon monoxide (CO) is another contaminant that has to be reduced to very low levels. The shift reaction using pressure swing absorption to remove CO can produce high purity H_2; however, the blow-down stream loses 10% or more of the fuel input. In large plants this can be

used for process heat; in smaller plants such use is more limited. Thus, the net efficiency of a reformer-shift reactor train is estimated at 75% for large installations and 60% for smaller ones. In this context, small refers to plants that produce at least 1 million scf of methane per day, which is equivalent to over 30,000 cows.[2] For a dairy manure facility with 5,000 cows, the best likely net efficiency would be around 50%. This does not consider parasitic energy requirements, which, again, can be high at small scales.

At present and for the foreseeable future, the real limitation of biogas-to-CH_4-to-H_2 conversion systems is the undeveloped nature of the technology, from production to storage to use. This is illustrated from the recent opening in Washington D.C. of the first H_2 fueling station, which uses liquid H_2, not on-site reformed H_2. Based on efficiency alone, conversion of biogas to biomethane to H_2 is perhaps the least favorable option for upgrading biogas.

Converting Biomethane to Liquefied Biomethane

Theoretically, biomethane from biogas can be liquefied to a fuel similar to LNG, which we call liquefied biomethane (LBM) in this report. This requires a combination of high pressures and low temperatures, and is a rather energy intensive and expensive process. However, emerging technologies developed in the last five years have highlighted better opportunities for LBM technologies. The advantages of LBM over CBM is a much higher energy content per volume, about 84,000 Btu/gallon or about 70% that of gasoline. If the energy required for liquefaction is ignored, 1,000 scf of CH_4 will yield about 12 gallons of LBM (if included, the yield is about 10 gallons/1,000 scf). Thus, assuming 10% losses and a separate source for electricity, a 1,500-cow dairy farm, producing about 70,000 ft^3 per day of biogas (45,000 ft^3/day of CH_4) could generate roughly 500 gallons of LBM/day.

However, as with other biogas upgrading options, there are a number of constraints on the conversion of biogas to LBM. First, the biogas needs to be meticulously purified, as even slight impurities (H_2O or CO_2) can cause significant problems during the liquefaction process (e.g., deposits on heat exchange surfaces, clogging of piping, etc.). Inclusion of air must be carefully avoided, as entrained O_2 would create danger of explosions (which is perhaps more of a problem with landfill gas, where air entrainment is common). Until quite recently, the capital and operating costs of the compression and liquefaction technology have been quite scale sensitive, with trade-offs between efficiency and costs.

---

[2] There are actually quite a number of small plants that convert methane (natural gas) to H_2 for industrial applications, primarily for use in refineries to remove H_2S and to clean up gasoline and diesel fuel. Typically, these systems have high available pressure and high purity natural gas and the product, H_2, has higher value as a chemical than it does as fuel.

Although large, centrally located LNG facilities are more economical in most respects than small dispersed production, small facilities do not have the added costs of distribution, storage, and associated losses, which can be significant for LNG. Many "stranded" natural gas wells and fields that are not serviced by pipelines would seem to be appropriate for the use of small-scale LNG production, which would allow the recovery natural gas that is currently flared. However, at the present time in California, only a single experimental Pacific Gas and Electric Company (PG&E) plant produces LNG, and this plant uses non-biomass sources for LNG production. All other LNG is imported from out-of-state, particularly from Arizona. This would seem to argue against the viability of small-scale production of LBM (or LNG) at present.

Several small-scale methane liquefaction technologies have been developed over the years. These include the following:

- *Anker-Gram liquefier*. More than 30 years ago, a Vancouver, Canada, company developed a 500-gpd system called the Anker-Gram liquefier for small-scale production of LNG for fueling vehicles. Although it is no longer in use, the technology (and, apparently the prototype liquefier unit itself) passed through many companies and traveled to many continents (North America, Australia, South America) over the years, demonstrating the feasibility of the technology along the way. It failed in the hands of Ecogas in Houston, Texas, because the "feedgas pressure was lower and CO_2 content higher than the liquefier was designed for." Powers and Pope (2002) state that this liquefier was "noteworthy because it is the only small liquefier that we know that has ever operated routinely to provide fuel for an LNG fleet."
- *Other relatively small units* (1,500 to 5,000 gpd from natural gas) have also been developed and tested in California. Liberty Fuels, Inc. had a liquefier proposed for use in the 250-to-2,000 gpd range, with a projected cost of $420,000 for operations of 1,000 gpd. However, only a 50-gpd pilot-scale unit was built. Powers and Pope (2002) state that "The liquefier is no longer in operation and it is unclear if Liberty fuels is still actively promoting onsite liquefiers and fueling stations at this time." More recently, the California Energy Commission (CEC) has supported development and demonstration of small-scale liquefaction units that could be used at stranded gas wells and landfill gas and could also be considered for dairy manure biogas.
- *A process developed by the Gas Technology Institute* (GTI) to produce 1,000 gpd of LNG from biogas or digester gas uses off-the-shelf components and has a purchase price of $150,000. Two important reservations are that the equipment purchase cost does not include gas cleanup cost and is only suitable for pipeline gas. If installation and cleanup are included, it is estimated by the project team that a system producing 1,000 gpd LNG would probably cost in the range of $500,000 to $1 million (Wegryzn, 2004)
- *A process attempted by Cryofuels, Incorporated* (Monroe, Washington) was supported at the Hartland Landfill in British Columbia. Problems were encountered with CO_2 freezeout, and the unit, despite later participation by Applied LNG technology, Inc. was ultimately shut down for lack of funding (Powers and Pope, 2002).

Despite its problems, the most apparently relevant project is that of CryoFuel Systems, Inc., of Monroe, Washington. In partnership with Applied LNG Technologies (ALT) a natural gas company, CryoFuel demonstrated a skid-mounted, 225-gpd liquefaction system at the Hartland

Road Landfill in Victoria, BC (Canada). The unit, shown in Figure 3-7, was reported to include a gas purification system (condenser and activated carbon unit) and CO_2 removal in dual-freezing heat exchangers followed by a temperature-swing absorber bed. The company has announced several projects for applying this process, including one in Kern County and one near Stockton, for both landfill gas and stranded gas wells. The Stockton project is said to have produced over 5,000 gallons of LNG per day beginning in 2003, but verification of actual long-term performance is lacking (Powers and Pope, 2002).

This recent activity indicates that technology for liquefaction is becoming more cost-effective Also, much of the lack of progress or success has been due to oil prices that were, until recently, low even in comparison to earlier inflation-adjusted prices. Now that oil prices have reached new

Figure 3-7 Skid-mounted 225-gpd landfill gas liquefaction Hartland Unit, located in Victoria, B.C. developed by CryoFuels Systems, Inc. (source: CryoFuels Systems, undated)

heights, continued improvements in this technology are likely. Carefully engineered demonstration projects can help achieve such advances.

Even so, the economics of the entire package (digester, LBM production unit, storage-fueling system, and vehicular modifications) would need to be investigated in some detail. From this initial review, however, liquefaction appears to be the most promising use for biogas. One of the advantages of LBM is that it is more easily distributed (via cryogenic tankers) than CBM, as discussed in Chapter 4. Although liquefaction is more challenging and expensive from a technological perspective than compression, it results in a more usable and more transportable product.