Purification Technologies for Biogas Generated by Anaerobic Digestion

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Background

Biogas is produced in many different environments, including in landfills, sewage sludge and during anaerobic degradation of organic material. Biogas is comprised of methane (CH_4, about 45-75% by volume), carbon dioxide (CO_2, 25-55%), and other compounds including hydrogen sulfide (H_2S, present in concentrations from several hundred to a couple of thousand parts per million), water, and other trace gas compounds. Methane is a powerful greenhouse gas if emitted into the atmosphere, but can also represent a valuable renewable energy source, with the potential to reduce GHG emissions when it is collected and substituted for fossil fuels.

Biogas can be used directly to generate power, but the large volume of CO_2 reduces the heating value of the gas, increasing compression and transportation costs and limiting economic feasibility to uses that occur at the point of production. Purification allows for a wider variety of uses, either for heat and electricity, or for vehicle fuels. For use as a fuel, purification to remove carbon dioxide (CO_2) and hydrogen sulfide (H_2S) is required, because H_2S corrodes vital mechanical components within engine generator sets and vehicle engines if it is not removed.

Purified biogas provides reductions in GHG emissions as well as several other environmental benefits when used as a vehicle fuel. Biogas emits less nitrogen oxide, hydrocarbon and carbon monoxide than gasoline or diesel, and engines fueled by purified biogas are quieter than diesel engines. Refueling with biogas presents fewer environmental risks than refueling with gasoline or diesel, because it can be done at small units located at an owner's home or business, minimizing the potential impacts if leaks or spills occur. Potential negatives include the high cost ($3-6/GJ) to upgrade the biogas, reduced driving range for vehicles dependent on specialty fuel, and less cargo space due to biogas storage.

Feasible biogas purification technologies exist for large-scale sewage and biowaste digesters, and the technologies for upgrading biogas, compressing, storing and dispensing biomethane are well developed. If cost-effective methods for upgrading biogas could be developed for the farm-scale, biogas purification could provide dairy farmers with revenue to complement (or replace) electrical power sales. This is especially critical in the Pacific Northwest, where low power rates have prevented cost competitive power from farm-scale anaerobic-digesters, limiting total dairy-derived power.

Engine conversion to accommodate biogas also represents a potential barrier, but because biogas has the same properties as natural gas, it can be easily used by vehicles which are configured for natural gas. Worldwide, there are about 10,000 biogas driven cars and buses, plus an additional 3.8 million natural gas fuelled

vehicles (representing 0.5% of the world vehicle stock), mainly in Argentina, Brazil, Pakistan, Italy, India and the U.S. (ENGVA, 2004).

To help develop appropriate biogas purification technologies for farm-scale anaerobic digesters, Washington State University evaluated various methods for removing acidic impurities, and developed and tested absorption tower technologies for application to a farm-scale anaerobic digester. In addition, Western Washington University has begun the process of building a full-scale pilot system. This pilot system will purify biogas from Vander Haak Dairy (Lynden, Washington), and sell it to Airporter Shuttle/Belair Charters for use by buses running along the Interstate 5 "Green" corridor from the Seatac airport south of Seattle to Ferndale, north of Bellingham. This is a new project for the diary industry, fuel users, and the community, as there is currently only one operational dairy-derived biomethane for transportation facility in North America, at the Hilarides Dairy in Lindsay, California, which began operation in the summer of 2009.

Evaluation of Existing Biogas Purification Technologies (Washington State University)

A review of existing technical solutions for scrubbing CO_2 and/or H_2S was carried out to identify the most promising options for application to farm scale anaerobic digesters. Existing technologies are summarized below with their major strengths and weaknesses.

Water and Polyethylene Glycol Scrubbing

Water scrubbing is used to remove CO_2 and H_2S from biogas since these gases are more soluble in water than methane. The absorption process is purely physical. Usually the biogas is pressurized and fed to the bottom of a packed column while water is fed on the top and so the absorption process is operated counter-currently (Figure 9.1). Water scrubbing can also be used for selective removal of H_2S since H_2S is more soluble than carbon dioxide in water. The water which exits the column with absorbed CO_2 and/or H_2S can be regenerated and re-circulated back to the absorption column. Regeneration is accomplished by de-pressuring or by stripping with air in a similar column. Stripping with air is not recommended when high levels of H_2S are handled since the water quickly becomes contaminated with elementary sulfur which causes operational problems. When cheap water can be used, for example, outlet water from a sewage treatment plant, the most cost efficient method is not to re-circulate the water.

Polyethylene glycol scrubbing relies on the same underlying mechanism as water scrubbing, with a physical absorption process that works because both CO_2 and H_2S are more soluble than methane in the solvent. Selexol is the trade name for one of the common solvents used for this process. The big difference between water and solvents is that CO_2 and H_2S are more soluble in Selexol which results in a lower solvent demand and reduced pumping. In addition, water and halogenated

hydrocarbons (contaminants in biogas from landfills) are removed when scrubbing biogas with Selexol. Selexol scrubbing is always designed with recirculation. Due to formation of elementary sulfur stripping the Selexol solvent is normally done with steam or inert gas rather than with air. Removing H_2S beforehand is an alternative.

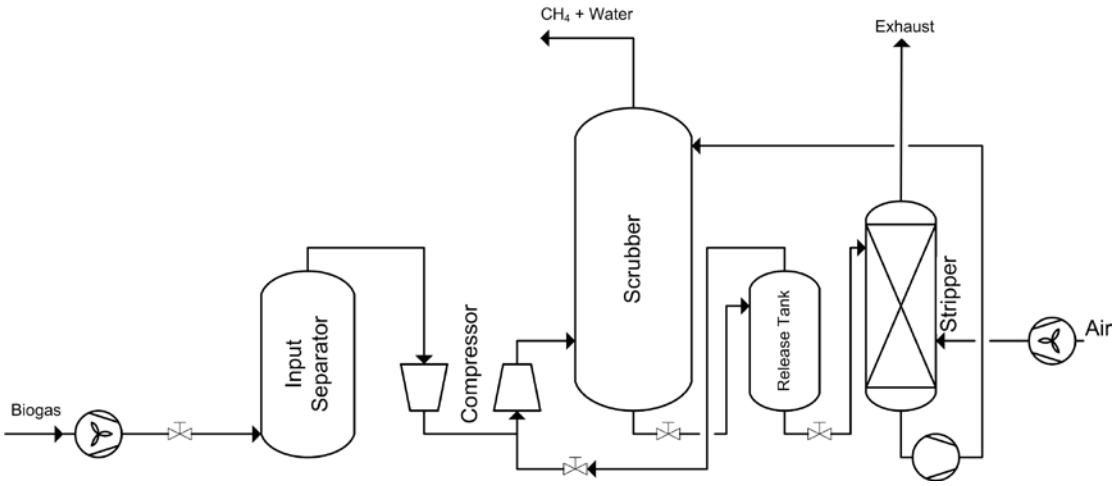


Figure 9.1: Flow chart of water scrubbing technology

The advantages of scrubbing are no special chemicals required (except relatively inexpensive glycol) and removal of both CO_2 and H_2S. The disadvantages of water scrubbing are that it requires a lot of water even with regeneration, as well as limitations on H_2S removal, because the CO_2 decreases pH of the solution and corrosion to the equipment caused by H_2S. According to De Hullu et al. (2008), the cost of the water scrubbing method is 0.13 €/Nm^3 biogas.

Chemical Absorption

Chemical absorption involves formation of reversible chemical bonds between the solute and the solvent. Regeneration of the solvent, therefore, involves breaking of these bonds and correspondingly, a relatively high energy input (Figure 9.2). Chemical solvents generally employ either aqueous solutions of amines (i.e. mono-, di- or tri-ethanolamine) or aqueous solution of alkaline salts (i.e. sodium, potassium and calcium hydroxides).

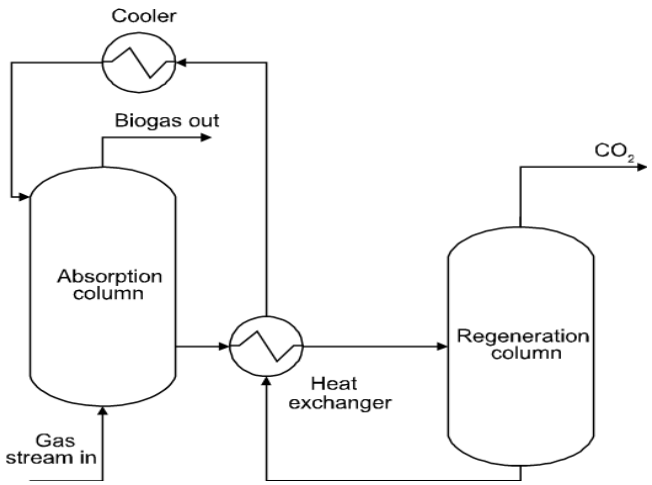


Figure 9.2: Flow chart of chemical absorption process

Biswas et al. (1977) reported that bubbling biogas through a 10% aqueous solution of mono-ethanolamine (Nelder and Mead) reduced the CO_2 content of biogas 40 to 0.5–1.0% by volume. MEA solution can be completely regenerated by boiling for 5 min and is then ready for re-use. The advantages of chemical absorption are complete H_2S removal, high efficiency and reaction rates compared to water scrubbing, and the ability to operate at low pressure. Because of these advantages, the process is commonly used in industrial applications, including natural gas purification (Kim et al., 2004; Palmeri et al., 2008). The disadvantages are the additional chemical inputs needed and the need to treat waste chemicals from the process. The final price of upgraded biogas using this technique is estimated to be €0.17 per Nm^3 biogas, according to De Hullu et al. (2008).

Pressure Swing Adsorption

Pressure Swing Adsorption (PSA) is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material (Figure 9.3). It operates at near-ambient temperatures and so differs from cryogenic distillation techniques of gas separation. Special adsorptive materials (e.g., zeolites and active carbon) are used as a molecular sieve, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbent material (Cavenati et al., 2005).

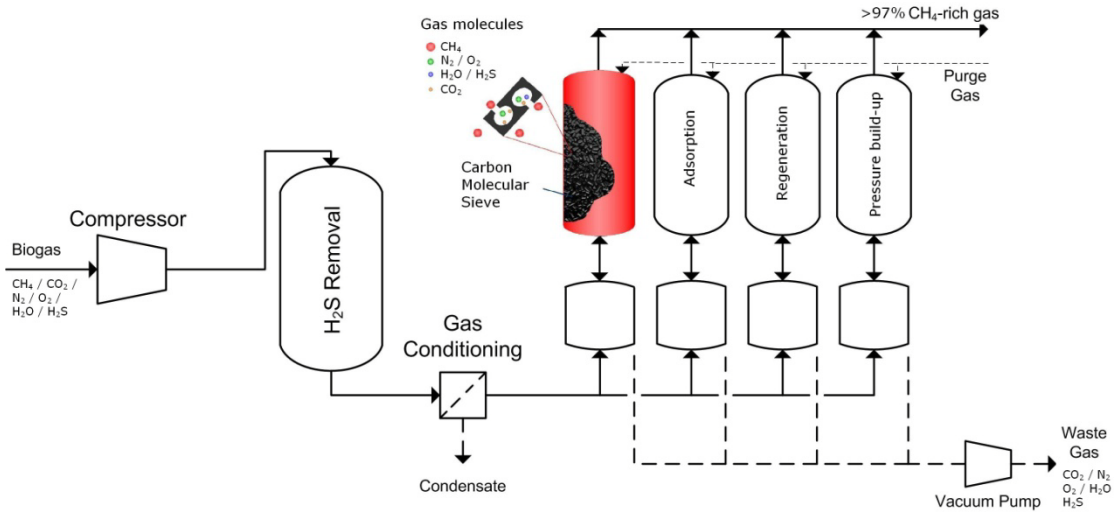


Figure 9.3: Pressure-swing adsorption schematic

The PSA process relies on the fact that under pressure, gases tend to be attracted to solid surfaces, or "adsorbed". The higher the pressure, the more gas is adsorbed; when the pressure is reduced, the gas is released, or desorbed. PSA processes can separate gases in a mixture because different gases tend to be attracted to different solid surfaces more or less strongly. If a gas mixture such as air, for example, is passed under pressure through a vessel containing an adsorbent bed that attracts nitrogen more strongly than it does oxygen, part or all of the nitrogen will stay in the bed, and the gas coming out of the vessel will be enriched in oxygen. When the bed reaches the end of its capacity to adsorb nitrogen, it can be regenerated by reducing the pressure, thereby releasing the adsorbed nitrogen. It is then ready for another cycle of producing oxygen enriched air. However, during biogas purification, the adsorption material adsorbs H_2S irreversibly and thus is poisoned by H_2S. For this reason a preliminary H_2S removing step is often included in the PSA process.

PSA using zeolites or activated carbon at different pressure levels is an effective method for the separation of CO_2 from methane (Grande and Rodrigues, 2007; Pinto et al., 2008). Activated carbon impregnated with potassium iodide can catalytically react with oxygen and H_2S to form water and sulfur (Pipatmanomai et al., 2009). The reaction is best achieved at 7 to 8 bar (unit of pressure) and 50 to 70^{o}C. The activated carbon beds also need regeneration or replacement when saturated. The advantages of PSA technology are more than 97% CH_4 enrichment, low power demand, and low emission and removal of nitrogen and oxygen. The main disadvantage of PSA technology is an additional H_2S removal step needed before PSA. Also, tail gas from PSA still needs to be treated. The process is also relatively more expensive than some others; according to De Hullu et al. (2008), the cost of PSA method is 0.40 €/Nm^3 biogas.

Membrane

The principle of membrane separation is that some components of the raw gas are transported through a thin membrane while others are retained. The permeability is a direct function of the chemical solubility of the target component in the membrane. Solid membranes can be constructed as hollow fiber modules or other structures which give a large membrane surface per volume and thus very compact units (Figure 9.4). Typical operating pressures are in the range of 25-40 bars. The underlying principle of membrane separation creates a tradeoff between high methane purity in the upgraded gas and high methane yield. The purity of the upgraded gas can be improved by increasing the size or number of the membrane modules, but more of the methane will permeate through the membranes and be lost.

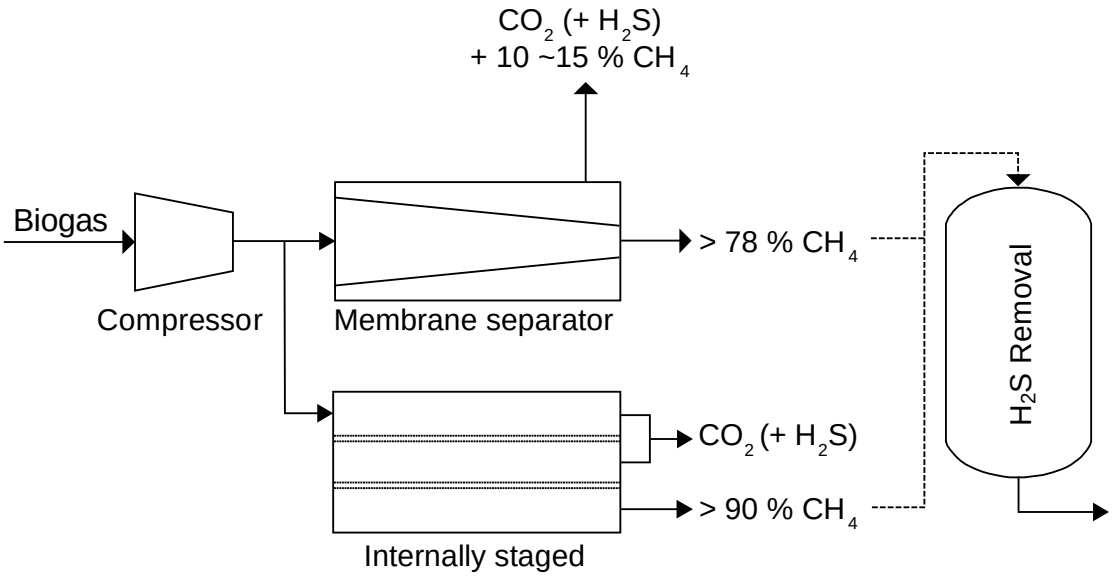


Figure 9.4: Flow chart of membrane biogas purification process

There are two membrane separation techniques: high pressure gas separation and gas-liquid adsorption. The high pressure separation process selectively separates H_2S and CO_2 from CH_4. Usually, this separation is performed in three stages and produces 96% pure CH_4. Gas liquid adsorption is a newly developed process that uses micro-porous hydrophobic membranes as an interface between gas and liquids. The CO_2 and H_2S dissolve into the liquid while the methane (which remains a gas) is collected for use (Chatterjee et al., 1997; Harasimowicz et al., 2007). The advantages of membrane separation are that the process is compact, light in weight, has low energy and maintenance requirements and easy processing. The disadvantages of membrane separation are relatively low CH_4 yield and high membrane cost. According to De Hullu et al. (2008), the cost of membrane method is 0.12 €/Nm^3 biogas. Although this cost is low in comparison to other methods reviewed, difficulties with yield and purity as well as the potential for fouling membranes (requiring membrane replacement) raises operating costs and strongly impacts project economics.

Bio-filter

Biological processes are widely employed for H_2S removal, especially in biogas applications. Because chemical use is limited, they are often economical and environmentally friendly (Duan et al., 2006; van der Zee et al., 2007). The use of chemotropic bacterial species (*Thiobacillus* genus) to condition biogas is well established. Microalgae cultures have also been examined but the available literature is short and cannot help in appropriately evaluating this option. Another methodology deploys anaerobic phototrophic bacteria (*Cholorobium limicola*) capable of oxidizing H_2S in the presence of light and CO_2. No known commercial applications at this time use phototrophic bacteria. The following text therefore focuses on chemotrophic bacteria.

Chemotrophic thiobacteria can purify H_2S in both aerobic and anaerobic pathways. Most thiobacteria are autotrophic, consuming CO_2 and generating chemical energy from the oxidation of reduced inorganic compounds such as H_2S. These processes commonly produce SO_4^{2-} and S^0 as waste products. On the other hand, some thiobacteria (i.e., *Thiobacillus novellus, Thiothrix nivea*) can grow either heterotrophically or autotrophically, having the capability of using available organic material as carbon source (i.e., glucose, amino acids). Biogas, which contains around 30% CO_2, is a good source of inorganic carbon, rendering it more suitable for autotrophic bacteria. Under limited oxygen conditions, *Thiobacillus* bacteria evoke a redox-reaction which produces S^0 (Equation 1). Conversely, an excess oxygen condition will lead to SO_4^{2-} generation and, thus, acidification, as shown in equation 1.

$$H_2S \leftrightarrow H^+ + HS^- \text{ (dissociation)}$$

$$HS^- + 0.5O_2 \rightarrow S^0 + OH^- \quad (1)$$

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+$$

Chung et al. (1996) isolated *Thiobacillus thioparus* from swine wastewater. The bacteria were immobilized with Caalginate to produce pellet-packing materials for a lab-scale biofilter (5-cm diameter, 25-cm working length). Growth was optimum at pH 6–8 under facultative autotrophic and heterotrophic conditions. The biofilter was operated under air-H_2S mixture flow between 36 to 150 L/h containing 5 to 100 ppmv of H_2S. Removal efficiency was more than 98% at residence times higher than 28 s. Optimal S-loading was 25 g m^{-3} h^{-1}. The main product was (i) S^0 (72%) at high H_2S concentration (60 ppmv), and (ii) sulfate (75%) at low H_2S concentration (5 ppmv). No pH fluctuation was observed. The experiments showed no temperature influence on removal efficiency between 20° and 37°C.

Thiobacillus ferroxidans, another potential bacterial species, is an example of a chemotrophic aerobe which can oxidize $FeSO_4$ to $Fe_2(SO_4)_3$. The resultant Fe^{3+} solutions are capable of dissolving H_2S and oxidizing it to S^0. This allows S^0 separation and permits biological $FeSO_4$ regeneration. These bacteria are acidophilic

and are able to grow at low pH levels (1 to 6). The main biochemical reaction is detailed in Equation 2.

$$2FeSO_4 + 1/2\ O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O\ (pH = 2) \quad (2)$$

Acidithiobacillus thiooxidans AZ11 has been isolated and incubated from H_2S-enriched soil (Lee et al., 2006). The bacteria can live in a very acidic environment, as low as pH = 0.2, with high sulfate concentration (74 g/l). A lab-scale biofilter (4.6 cm diameter, 30 cm working length) was inoculated with these inocula on a crushed, porous ceramic support. The study showed that, at a low flow rate (space velocity = 200 h/1) and residence time of 18 s, this species was capable of degrading high H_2S concentration (2200 ppmv) and S-loading of 670 g/(m3*h). Removal efficiency ranged from 94% to 99.9% and was demonstrated to be dependent on residence time (the studied range was 6 to 18 s).

Figure 9.5 shows a biological H_2S scrubber designed by Soroushian et al. (2006), consisting of a fiberglass tank packed with plastic media and a makeup water recirculation pump. With this system, H_2S levels were maintained at below the 40-ppmv target level by the scrubber under normal operating conditions, but low temperature and nutrient deficiency could lower microbial activity levels and resulted in a pH drop. The H_2S containing gas enters the absorption section and is washed by scrubbing liquid. The liquid has an alkaline nature (pH 8–8.5) and absorbs the H_2S. The biogas exits the top of the absorber virtually free of H_2S. The sulfide containing liquid flows into the bioreactor. In the reactor bacteria oxidize the sulfide with oxygen. The sulfur is then removed by use of a settler. The sulfide-free liquid returns to the absorption section.

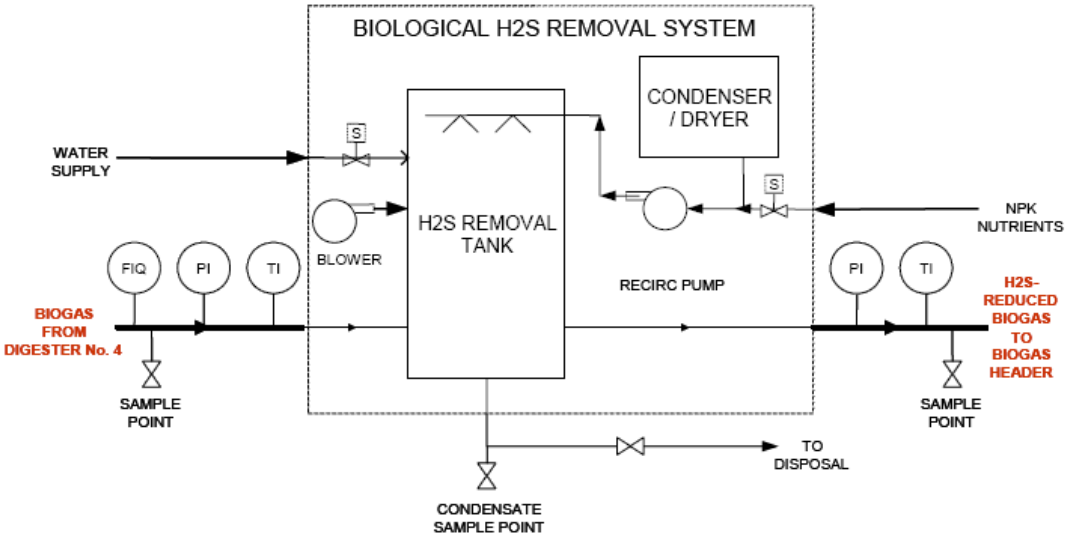


Figure 9.5: Biological H_2S removal system (Soroushian et al., 2006)

The advantages of biological methods are low energy requirement, mild conditions and the elemental sulfur byproduct. Sulfur can be re-used for the production of

sulfuric acid, hydrogen sulfide or agricultural applications (Kim et al., 2002; Vannini et al., 2008). Biological methods also have some disadvantages: additional nutrients are required for growing bacteria, and a small amount of O_2 and N_2 are left in treated biogas. The H_2S removal efficiency depends on the activity of bacteria. Bench-marking studies show that the method described above is cost effective up to 40 tons per day.

Cryogenic Separation

Cryogenic separation of biogas is based on the fact that CO_2, H_2S and all other biogas contaminants can be separated from CH_4 based on the fact that each contaminant liquefies at a different temperature-pressure domain. This separation process operates at low temperatures, near -100°C, and at high pressures, almost 40 bars. These operating requirements are maintained by using a linear series of compressors and heat changers (Figure 9.6).

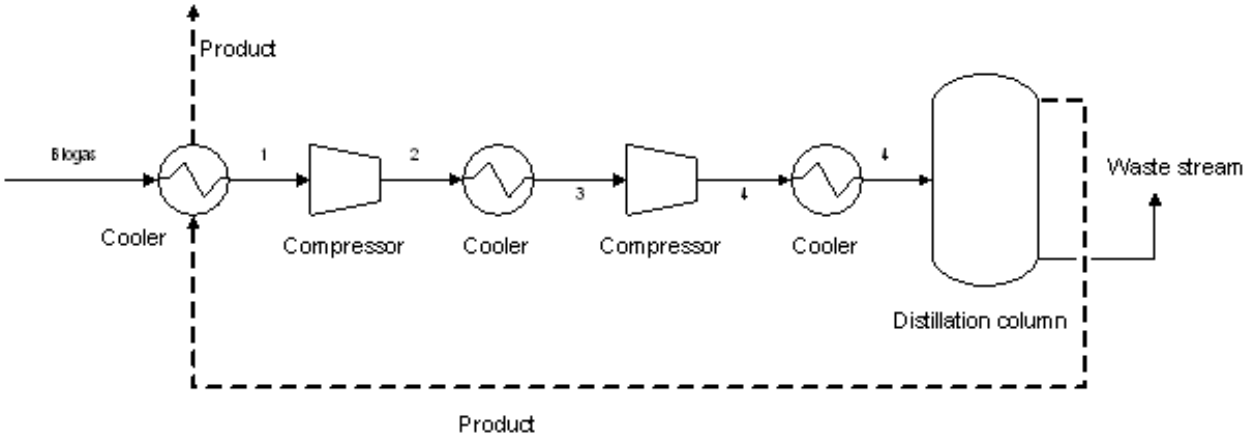


Figure 9.6: Schematic of cryogenic separation

Crude biogas streams through the first heat exchanger which cools the gas down to 70°C. This heat exchanger makes use of the product stream as cooling medium, which is energy efficient and has the advantage of preheating the upgraded biogas before leaving the plant. The first cooling step is followed by a cascade of compressors and heat exchangers which cool the inlet gas down to -100°C and compress it to 40 bars before it enters the distillation column. Finally, the distillation column separates CH_4 from the other contaminants, mainly H_2S and CO_2.

The main advantage of cryogenic separation is the high purity of the upgraded biogas (99% CH_4), as well as the large quantities that can be efficiently processed. The main disadvantage of cryogenic separation is that cryogenic processes require the use of considerable process equipment, mainly compressors, turbines and heat exchangers. The need for the equipment raises capital and operating costs relative to other options. The final price of upgraded biogas using this technique is estimated to be €0.44 per Nm^3 biogas (De Hullu et al., 2008).

Environmental Impact

The environmental impact of the upgrading processes is an important factor that can be used to compare the different techniques. If the pollutants that are removed from biogas during upgrading are emitted in the atmosphere, the contamination of the environment will run counter to the goal of producing an environmentally-friendly fuel to replace current fossil fuels. Environmental impacts for each process were therefore considered, with concerns summarized briefly below.

Chemical Absorption

The only process stream other than biogas needed in the absorption process is a liquid water phase containing a catalyst. This either can be amines for the absorption of CO_2 or Fe/EDTA complexes for the absorption of H_2S. During the upgrading process CO_2 is emitted in the atmosphere as a waste stream. The used amine solution must be replaced a few times a year and thus is also a waste. This solution can be separated into a water phase and the amines using a membrane. The clean water phase can then be purged to a river.

High Pressure Water Scrubbing

The water scrubbing process contains two main waste streams. The first waste stream is the exhaust of air which was used to strip the regenerated water. This stream mainly consists of air enriched in CO_2 but also contains traces of H_2S and CH_4. Because H_2S is rather poisonous, this stream needs to be treated. And because CH_4 is far more damaging to the environment than CO_2 the CH_4 in this stream should be burned. The second waste stream consists of water which is purged and replaced with clean water to keep dissolubility as high as possible and avoid accumulations of CO_2 and H_2S. Because most of the CO_2 and H_2S will be absorbed in the stripper during the gas phase the purge stream does not have to be treated.

Pressure Swing Adsorption

Besides the product stream (upgraded biogas, containing more than 97% CH_4), the pressure swing adsorption process creates a waste stream, which contains all the adsorbed material from the molecular sieves. Among other things, some significant amounts of CH_4 are found in this waste stream. Normally, the CH4 is burned to avoid emissions. Often, the waste stream leads to a gas engine linked to a generator. Alternatively, the waste stream can be recycled back through the adsorption process, which reduces the amount of CH_4 in the waste stream and increases the yield of CH_4 in the product stream.

Cryogenic Separation

The fact that cryogenic separation uses no chemicals makes this separation an environmental friendly technique, though the process uses considerable energy. The only waste stream consists of a high percentage of CO_2 with traces of H_2S and CH_4. As in other processes, because H_2S is rather poisonous and CH_4 is more damaging to the environment than CO_2, this stream needs to be treated.

Membrane Separation

The waste gas still contains CH_4 which is highly polluting. Part of it can be fed back into the inlet or, as in pressure swing absorption, the waste gas can be burnt in a gas engine linked to a generator. Using a multistage setup also increases the yield. Positive results have been found using an internally staged permeator. Electrical use is low since only a compressor has to be powered. The generator can power the compressor which results in an even higher CH_4 efficiency. The CO_2 stream is then of no further use.

Experimental Testing of Absorption Tower Technologies (Washington State University)

In addition to evaluating biogas purification technologies, WSU constructed and tested a laboratory-scale biogas purification tower based on the chemical absorption process.

Materials and Methods

A laboratory-scale biogas purification tower (3.5 m tall) was constructed (Figure 9.7) using $1.57x10^{-2}$ m^3 of BH-type packing. This packing was used to increase the transfer efficiency of carbon dioxide between simulated biogas and an amine working solution. The BH-type packing, shown in Figure 9.8, is characterized by chemically treated wave-like corrugated sheet surfaces with specific geometric areas ranging up to 2000 m^2/m^3 (Lei et al., 2009). The tower was operated in batch mode by spraying an amine working solution from the top through a distributor onto the packing material surface, allowing the working solution to contact the simulated biogas for a specific period of time, and then collecting the working solution at the bottom.

Biogas was simulated by combining methane cylinder gas with carbon dioxide cylinder gas in various ratios. The biogas, introduced at the bottom of the tower, flows up through the packing material, interacts with the amine working solution, and then flows out near the top. Thermocouples were installed at both the top and the bottom of the tower for monitoring of operating temperatures. Before each batch experiment, air was removed from the system using a nitrogen purge and then nitrogen was removed using the simulated biogas mixture. Gas samples were collected in vacuum polypropylene bags during the experiments. A baseline amine working solution sample was taken prior to beginning the experiment. Several amine types and concentrations were tested for their efficacy in removing CO_2 from the biogas.

Figure 9.7: Experimental biogas purification set-up.

Figure 9.8: BH-type packing material

Analytical Methods

Methane and carbon dioxide concentrations were analyzed using a Varian CP-3800 Gas Chromatograph (CP-3800, Varian, Walnut Creek, CA). Temperature and pH were measured according to Standard Methods (APHA, 1998).

Results and Discussion

The first batch of simulated biogas purification experiments used 40% MDEA as the absorbent at a simulated biogas flow rate of 120 L/min. The amine working solution flow rate was 2.0 L/min using a 6.0 L recycle reservoir. As shown in Figure 9.9a, carbon dioxide concentration decreased from 22% to 12% in the first 5 minutes. The pH of the solution dropped quickly from 11.67 to 10.0 in the first 5 minutes (Figure 9.9b). After the initial drop, pH slowly continued to descend from 10 to 9.1 over the next 35 minutes. With the BH-type packing materials, the pressure drop across the tower was 0.2 – 0.4 inch H_2O.

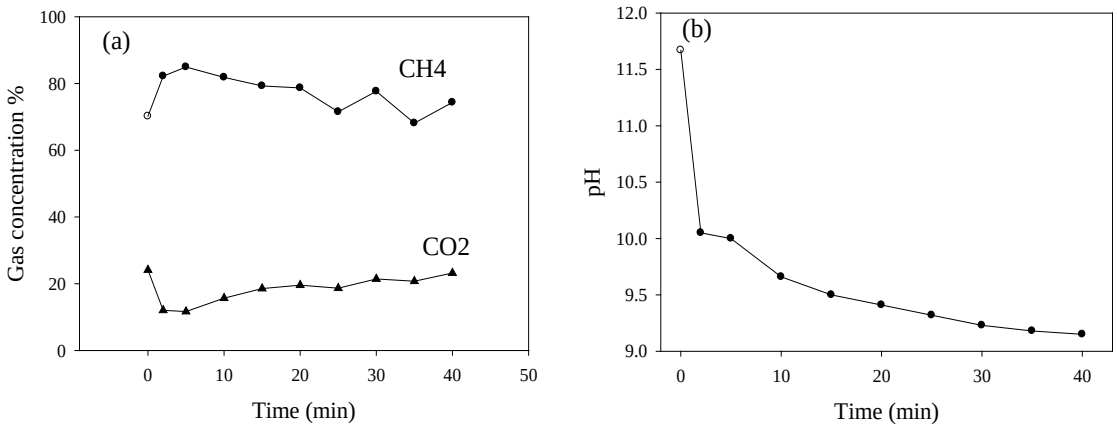


Figure 9.9: Biogas purification results with 40% MDEA.

The second batch of simulated biogas purification experiments used 20% MEA as the absorbent. The simulated biogas flow rate and the amine working solution flow rates were 90 L/min and 2.0 L/min, respectively. The experimental results are shown in Figure 9.10. Carbon dioxide concentration decreased from 27% to 0% over 2 minutes and stayed at 0% for 12 minutes. After 12 minutes the carbon dioxide concentration increased to 26%. It took about 15 minutes for the pH to drop from 12.3 to 9. Over the first 14 minutes of this batch experiment, the temperature of the absorbent increased from 28°C to 47°C (Figure 9.10c). The temperature of the biogas increased from 31°C to 43°C. After 14 minutes the absorbent was nearly saturated with carbon dioxide, the reaction rate decreased, and the temperature of the solvent decreased.

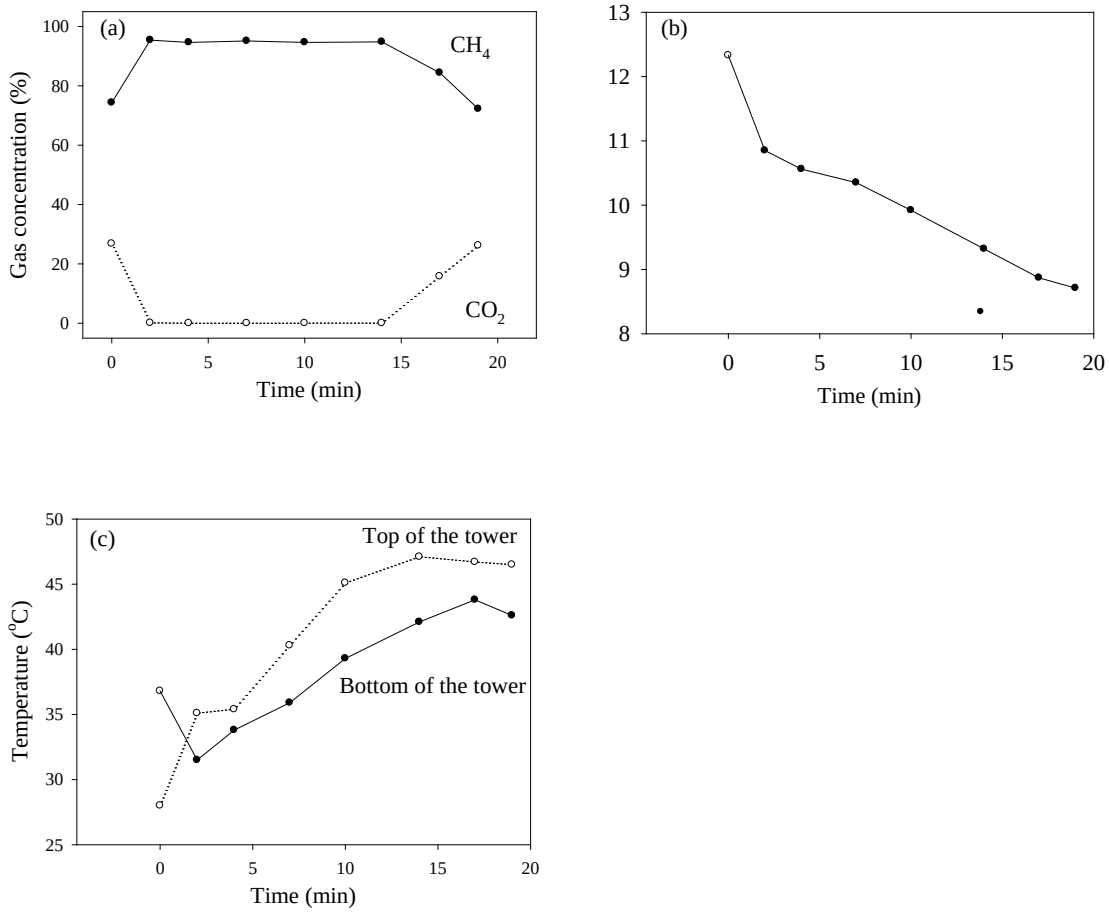


Figure 9.10: Biogas purification results with 20% MEA

The third batch of biogas purification experiments used 10% MEA solution as the absorbent (Figure 9.11). The simulated biogas flow rate and the amine working solution flow rates were 75 L/min and 1.6 L/min, respectively. The carbon dioxide concentration decreased from 32% to 0% in 1 minute. The carbon dioxide concentration remained at 0% for 7 minutes. After 7 minutes the carbon dioxide concentration increased to 30%. The temperature of the absorbent increased from 21°C to 42°C (Figure 9.11c). The temperature of the simulated biogas increased from 32°C to 38°C. After 8 minutes the absorbent was nearly saturated with carbon dioxide, the reaction rate decreased, and the temperature of the solvent decreased.

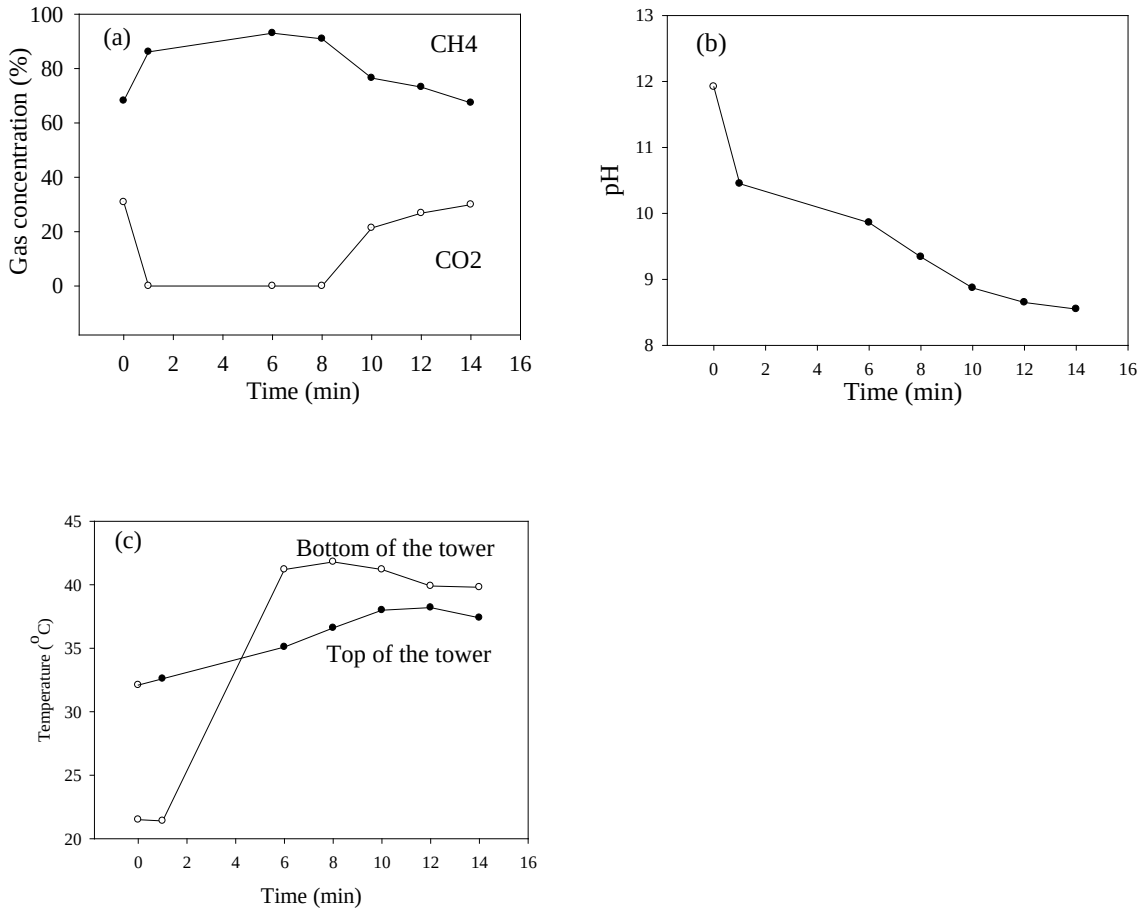


Figure 9.11: Biogas purification results with 10% MEA

As shown in Table 9.1, MEA showed better carbon dioxide removal efficiency than MDEA. Using 10% MEA as an absorbent resulted in 100% carbon dioxide removal. Hydrogen sulfide removal with amine absorption will be tested in the future. By using 10% MEA, CO_2 was completely removed in 1 minute. 100% removal can only be achieved before the amine solution approaches carbon dioxide saturation, which takes about 7 minutes; after 7 minute the pH falls to 9.5 and inhibits the reaction. With 20% MEA, carbon dioxide saturation takes 12 minutes. The absorption reaction is exothermic, and with the surface area provided by the BH-type packing material and the tower height that was used, the amine working solution temperature increased by 20°C.

Table 9.1: Results of biogas purification experiments with different absorbents

Amine	Amine flow rate (L/min)	Gas flow rate (L/min)	Biogas composition		CO_2 removal (%)	Time of max CO_2 removal (min)
			CH_4% (%)	CO_2% (%)		
40% MDEA	2.0	90	74	26	50	0
40% MDEA	2.0	60	79	21	67	0
40%MDEA +2%Piperazine	2.0	90	71	24	50	0
20%MEA	2.0	90	74	26	100	13
10%MEA	2.0	90	68	32	100	7
10%MEA	1.6	75	74	26	100	5
30% MDEA +10%MEA	2.0	90	74	25	100	5

Conclusion

The experimental results demonstrate that of the various amine solutions and amine concentrations tested, 20% MEA performed the best, successfully removing 100% of the CO_2. Further, results showed that pH can be an excellent indicator for amine saturation, thereby offering a technical approach towards optimizing reaction time and sequencing of absorption/desorption flows. Heat captured from the exothermic reaction could be used to reduce the heating costs required in the regeneration phase.

Within an overall systems view, this research confirms a potentially viable and economically preferable mechanism for biogas upgrade, be it for fuel production or simply improved engine/generator performance. Proprietary technology utilized by various AD providers has already been shown at commercial scale to be capable of reducing H_2S levels from the thousands of ppm to mere hundreds, mostly through the use of oxygen dosing mechanisms coordinated with the growth of H_2S oxidizing bacteria. The previously discussed ammonia stripping and recovery process (Chapter 8) has at its core approach, capabilities in simultaneously restoring effluent pH and preferentially scrubbing H_2S through the bubbling of raw digester biogas into the ammonia-treated effluent. Although only limited reduction on H_2S concentration was accomplished at high biogas to effluent liquid ratios (~40:1) and a starting H_2S concentration in the thousands of ppm, it can be inferred that if the starting concentration were dramatically reduced through oxygen dosing, subsequent ammonia treatment and pH control could produce a biogas nearly 100% removed of H_2S. If so, only subsequent CO_2 removal through amine treatment would be required, thereby reducing overall costs and complexity of utilizing scrubbing towers and systems designed to remove both CO_2 and H_2S.

Preliminary Pilot-Scale Trials of Biogas Purification (Western Washington University)

While WSU conducted targeted research on using chemical solvents to exclusively remove CO_2 as its integrated nutrient recovery process was designed to pre-treat the H_2S, WWU conducted its own pilot-scale research comparing two base methods for removing H_2S and CO_2. Beginning in 2004, Western Washington University's Vehicle Research Institute (WWU-VRI) surveyed two processes for upgrading biogas to biomethane, a sodium hydroxide system and a diethanolamine system.

Sodium Hydroxide System

The first system used sodium hydroxide because it reacts with both hydrogen sulfide and carbon dioxide but not with methane. A three tower system was constructed, consisting of a first stage with iron filings, a second stage with sodium hydroxide, and a third stage of desiccant. The first tower used a polyvinyl chloride (PVC) pipe with a 100 mm inside diameter and a 3 m height. The tower was packed with machine shop tailings of iron and steel, as hydrogen sulfide reacts with iron oxide to form iron sulfide. The biogas entered the tower from the bottom through a 19 mm hose. The second tower used a 300 mm inside diameter PVC pipe of 1.8 m height. A 10% solution of sodium hydroxide was sprayed from the top of the tower. Polyethylene balls of 25 mm provide a large surface area to increase the biogas/liquid interaction. The biogas rises from the bottom and the carbon dioxide reacts with the sodium hydroxide to form sodium carbonate. The third tower was 0.6 m tall and 250 mm inside diameter, and filled with desiccant to remove water vapor from the biogas. The biomethane was then compressed to 1700 psi and collected in storage tanks. An intermediate tank was used as an oil trap. The PVC construction is low cost and resistant to the corrosive effects of hydrogen sulfide. It was determined that epoxy was required to seal PVC seams and joints when dealing with raw biogas.

Analytical Methods

Biogas from the Vander Haak Dairy (Lynden, WA) anaerobic digester and the upgraded biomethane from the sodium hydroxide system were sampled in test bags. The bags were tested in the gas chromatograph at the Conoco Philips refinery in Ferndale, Washington.

Results and Discussion

The inlet biogas was roughly 60% methane, 40% carbon dioxide and 3500 ppm hydrogen sulfide. The sodium hydroxide system improved methane concentration from roughly 60% to 94%. The caustic solution corroded the spray system, which required cleaning after only two to three hours of operation. After six to eight hours, the caustic solution became saturated with carbon dioxide and was no longer able to remove hydrogen sulfide or carbon dioxide. Results of three testing periods are shown in Table 9.2.

Table 9.2: Sample results from the first refinery

Sample	Date	CH_4	CO_2	H_2S	N	O
Raw	4/28/2006	60.59%	36.03%	0.34%	2.50%	0.53%
1	4/28/2006	93.62%	2.05%	<1000 ppm	3.29%	0.77%
2	5/4/2006	57.38%	40.76%	<1000 ppm	1.52%	0.34%
3	5/4/2006	56.06%	41.76%	0.35%	1.48%	0.35%
Tank 1	5/5/2006	81%	15.03%	900ppm	2.26%	0.37%
Tank 2	5/5/2006	83.46%	11.51%	850ppm	2.97%	0.57%
Tank 3	5/5/2006	75.28%	14.54%	<1000 ppm	7.46%	1.47%

A sample of the raw biogas was taken prior to the refinery inlet. Samples 1 – 3 were taken at the outlet. Sample 1 was taken twenty minutes after system startup, whereas Samples 2 and 3 were taken after more than eight hours of operation and show the degraded performance of the system. Tank samples 1 – 3 show methane levels taken from the storage tanks at 100 bar pressure following compression. Hydrogen sulfide levels remain below 1000 ppm in all of the tests (except raw biogas). This may represent hydrogen sulfide reduction from the operation of an iron filing tower alone. The sodium hydroxide appeared to be loaded with carbon dioxide during most of the tests.

Conclusion

Although team was encouraged by the initial test results, the results shown above indicate that the sodium hydroxide system is not appropriate for a refinery, as the need for continuous addition of sodium hydroxide solution seems unworkable. In addition, the gas with ~900 ppm hydrogen sulfide stored in tanks over a three month period caused tank valves to seize, ultimately requiring replacements.

Diethanolamine System

Two subsequent pilot refinery units relied on amine-based recovery, which ultimately was combined with a biological process. It is hoped that this will result in lower costs for biogas upgrading.

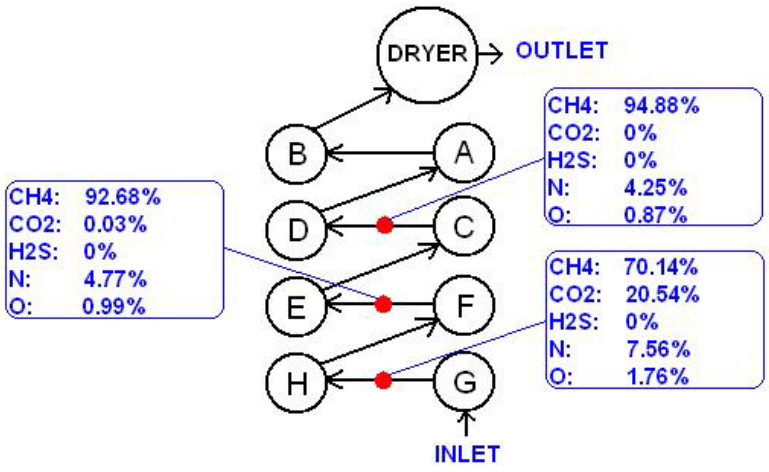
The first diethalanolamine system was constructed to be transportable (to meet the requirements of the EPA People, Prosperity, and Planet award competition held in Washington D.C.). After a design phase and a physical mock-up, the second refinery was built with eight, 2 m long PVC tubes of 100 mm inside diameter. The tubes were arrayed vertically in a two by four pattern as viewed from above. High surface area polyethylene balls, injection molded by students, filled each tower. A 19 mm diameter fitting at the bottom of the first tube allowed raw biogas to enter. The biogas traveled upward through the 25 mm polyethylene balls in the first tower and then downward to the next tube in a 19 mm high velocity connector tube. A total of 200 liters of DEA solution was sprayed from the top of each tube at a rate of 4 to 10 liters per minute. Gas sampling ports were built into the system after the first tube

and then after every second tube. Four sampling ports were provided between the tubes.

Analytical Methods

Samples were taken and analyzed at the BP Cherry Point refinery gas chromatograph. Results are shown in Figure 9.12.

Figure 9.12: Second refinery results, April 3, 2007



Results and Discussion

These results showed that H_2S was eliminated following the first tube, labeled G in Figure 9.3. Carbon dioxide was nearly eliminated after the third tube, labeled F. Results of 0% represent the lower level of sensitivity and indicate a content below 100 ppm. An additional test was performed to analyze the outlet gas performance. Table 9.4 below shows these final results below:

Table 9.3: Refinery outlet results, April 10, 2007

Sample	Time	CH_4	CO_2	H_2S
Outlet	4:08 p.m.	92.36%	0.01%	0%
Outlet	4:12 p.m.	95.46%	0.01%	0%
Outlet	4:15 p.m.	97.81%	0.01%	0%

Nitrogen was used prior to testing as a purge gas to remove oxygen from the system. As the nitrogen left the system, methane levels rose. Tests performed with Druegger tubes indicated levels of hydrogen sulfide below 10 ppm in the outlet gas with low levels of carbon dioxide. Both of these levels are upper requirements for any refinery system used to produce vehicle fuel. The test results demonstrate the effectiveness of the DEA-based solution. Several other adsorption solutions exist;

some may prove superior to DEA. DEA was chosen due to its ability to absorb large quantities of carbon dioxide and still adsorb hydrogen sulfide.

Conclusion

Although the system successfully upgraded biogas, several operational challenges remained, that are being addressed in a farm-scale pilot system being installed at VanDerHaak Dairy in Lynden, WA. Specifically, the design of the system (with eight separate 2 m towers) created issues with pressure drops, and difficulties in balancing the flow and fluid levels in each tower. Unfortunately, the DEA working solution pump was directly plumbed to a spray head at the top of each tube. Each spray head could be individually throttled, but there was no return line from the spray head array to the DEA sump. As a result, attempts to reduce and balance the flow at each spray head led to an increase in system pressure, and ultimately, leaks and joint failures. These design issues were addressed in the third refinery unit, designed for pilot scale operation.

Pilot-Scale Biogas Purification (Western Washington University)

The full pilot-scale refinery unit attempted to address the design limitations discovered in the previous design, as well as to create a method for regenerating the DEA and fully treat the waste streams resulting from the process. The refinery was built at the same dairy in Lynden, WA where the initial anaerobic digester was installed and tested, adjacent to the anaerobic digester. The current target is to operate an Airporter Shuttle/Bellair Charter bus on biomethane.

The pilot scale refinery unit is currently in construction. It is designed to produce 25 scfm of refined biomethane at nearly 250 bar (3600 psi) for storage in tanks. The system will have provisions for both fast fill and time fill operations. The refinery design target could support up to 16 large buses or nearly 170 vehicles. Storage capacity and amine regeneration rates will initially limit production to support up to five large buses. The unit consists of two 6 m towers with 300 mm inside diameter. A DEA working solution sprays from the top of each tower onto a collection of high surface area elements. Biogas enters each tower from the bottom. A 12 m (40 ft) double door shipping container is used to house two 28 scfm compressors, an amine regeneration unit, and a bioreactor system for processing hydrogen sulfide and carbon dioxide. A control room will manage process flows automatically with a programmable logic control system. Racks of DOT cylinders will be stored on the top of the container. The entire system sits on a concrete pad roughly 6 m by 12 m. The system meets or exceeds all existing codes, especially NFPA 52.

To enable the design of the pilot scale refinery, three different investigations were performed. The first was a material study to analyze the corrosive effects of DEA solutions loaded with hydrogen sulfide and carbon dioxide. The second was a study of an amine regeneration unit, and the third was testing involving bioreactors. The use of the bioreactor is novel and requires protection from public disclosure.

The material study focused on grade 316 stainless steel, PVC, and chemically resistant fiberglass composite as potential materials for the main refinery towers. Samples of each material were prepared and submerged in corrosive solutions for varying lengths of time. The samples were observed under a scanning electron microscope and compared with samples that were not submerged. All three materials showed minimal damage. The fiberglass was the least damaged and was chosen for the 6 m tubes over stainless steel as a result of this test and the significant cost savings achieved. The material study guided the selection of all refinery related materials. Grade 316 stainless steel pipe in 25 mm diameter is used for all DEA lines while polyethylene (PE) will be used for some lines as well. The challenge with PE is the difficulty of forming corrosion resistant joints.

An amine regeneration unit was built in small scale to demonstrate the feasibility of regeneration. The process is used in oil refineries to remove hydrogen sulfide from gas streams. The Klaus process is then used to process the hydrogen sulfide. Remaining hydrogen sulfide is then oxidized in a furnace. For the biomethane refinery, the Klaus process was deemed too complex and expensive at small scale and the furnace entirely unacceptable from an emission point of view. The regeneration unit is still required to reuse the amine solution and separate the hydrogen sulfide and carbon dioxide. The test unit is designed to have an amine solution enter a heat exchanger to heat up the incoming solution and reject heat from the outgoing solution. The amine working solution passes through a heating vessel, where 10,000 BTU propane burners heat the vessel. As the amine solution approaches 100^{o}C, the hydrogen sulfide and carbon dioxide de-adsorb and rise to a vent. The amine solution passes back through the heat exchanger and returns to the amine solution sump. A motor controller was designed and fabricated at WWU to control a pump for the amine solution that operates prior to the heat exchanger on the inlet side. The vapor that leaves the heating vessel travels through a 2 m tube with a 200 mm inside diameter, filled with polyethylene balls. A solution of sodium hypochlorite sprays down upon the tower and polyethylene balls to react with the hydrogen sulfide. The remaining gas travels through an iron-filing-filled tube to remove any remaining hydrogen sulfide, while the carbon dioxide is allowed to pass through. As of April 1, 2010, construction of the pilot facility was nearing completion.

Getting the upgraded biogas to the end user has also presented some challenges. Ultimately, the upgraded biogas should ideally be injected directly into an existing natural gas pipeline system or (as a less-preferred solution) be hauled by tanker. However, for this initial pilot study, a refueling rig will take biogas from the farm in Lynden to the Airporter Shuttle/Bellair Charter bus depot in Ferndale, roughly 17 miles away. (Concerns with border traffic made it infeasible for buses to fuel directly at the farm.) The refueling rig has wiring for a generator and space for a mobile natural gas compressor. It can hold up to ten compressed natural gas tanks, with a capacity of more than 200 GGE. The vehicle has been purchased, and the necessary conversions are in the process of being completed.

Unfortunately, the use of a refueling rig adds complexity and cost to the pilot project. As a tank array is used to fill a CNG vehicle's fuel tank, the two fuel systems come to pressure equilibrium. At this point, no further gas will flow into the CNG vehicle's fuel tank and a significant quantity of fuel will remain in the storage tank array. Typically up to 40% of the fuel in the storage array may not be used. To address this issue requires either larger storage facilities or a booster compressor that regulating the fuel pressure down to an inlet pressure of a pump before compressing it back into a vehicle tank. Either solution is costly, requires additional space and weight on a mobile vehicle and uses additional energy for the booster pump. This challenge would not occur if the vehicle could be fueled at the farm, where the compressor could be used to top off the vehicle.

Due to a variety of constraints on the way the funding for the vehicle can be spent, the vehicle chosen to run on upgraded biogas is a 2000-2003 year MCI F coach bus. Conversion will be completed by Cummings Northwest. In addition to this bus, a Ford E250 bi-fuel van, with both gasoline and natural gas capability, was purchased and will be updated with a compressed natural gas fuel injection.

Finally, beyond the technical challenges, the team is providing assistance to develop the contract between the dairy and Airporter Shuttle/Bellair Charters for biogas purchase and delivery. The team is leveraging experience gained from other local governments in buying and selling biomethane. The team is also working with the Whatcom Public Utility District No. 1.

Conclusion

Though technical obstacles remain, the team has made considerable progress towards implementing a pilot-scale biogas purification facility next to a farm-scale anaerobic digester. Overcoming the challenges continues to generate lessons that will be helpful to others aiming to implement similar technologies. Through the additional revenue generated, biogas purification technologies have the potential to improve the economic feasibility of anaerobic digestion, particularly in the Pacific Northwest, where prices received for electricity generation are relatively low because of the abundance of cheap hydroelectric power in our region.

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