Characterization of Dairy-Derived Biogas and Biogas Processing

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Abstract. Anaerobic digestion offers an effective way to manage dairy manure by addressing the principal problems of odor and environmental control while offering an opportunity to create energy from conversion of biogas with a system of combined heat and power (CHP). The use of biogas as an energy source has numerous applications. However, all of the possible applications require knowledge about the composition and quantity of constituents in the biogas stream. This study provides data on composition of anaerobic digestion biogas (ADG) over time (hourly, daily, weekly and year), results from the use of dairy-manure compost as a biofilter to remove hydrogen sulfide (H₂S) and an assessment of the feasibility of injecting ADG into the natural gas pipeline.

Results agree well with often quoted generalized concentrations of 60% CH₄, 40% CO₂ and 600 BTU/ft³ for dairy-derived biogas. Also shown, depending on additives to the dairy manure and quality of farm water supply, H₂S concentrations can vary substantially from less than 1000 ppm to well over 6000 ppm. Utilization of cow-

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manure compost for removal of $\text{H}_2\text{S}$ from AD biogas, using small-scale reactors, was studied and shows promise. A technical and economic assessment of processing of biogas for injection to the natural gas pipeline, while dependent on biogas quantity, price for processed biogas, proximity to the natural gas pipeline and the interest rate, suggests that a real possibility exists for injecting biogas into the natural gas pipeline dependent, of course, on the values of the parameters indicated.

**Keywords.** dairy manure-derived biogas, biogas composition, biogas cleanup, hydrogen sulfide removal, injection of biogas to natural gas pipeline
Introduction

Anaerobic digestion is a microbiological process that produces a gas, biogas, consisting primarily of methane (CH₄) and carbon dioxide (CO₂). The use of biogas as an energy source has numerous applications. However, all of the possible applications require knowledge about the characteristics, composition and quantity of constituents in the biogas stream.

This project provides information about the fundamental characteristics of biogas. By better understanding its components, biogas can be processed and utilized in a more efficient, cost-effective way. As shown in Figure 1, biogas contains primarily CH₄ with the balance being mostly CO₂ and a small amount of trace components. In comparison, biogas has approximately two-thirds the energy potential of refined natural gas. Although the significant amount of CO₂ and lower CH₄ means a lower energy value than natural gas, the relatively minute concentrations of trace components can also have a particularly complicating and deleterious effect on the way biogas can actually be processed and utilized.

<table>
<thead>
<tr>
<th>Typical Components</th>
<th>Biogas</th>
<th>Trace Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane 50-60%</td>
<td>Hydrogen</td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide 38-48%</td>
<td>Hydrogen Sulfide</td>
<td></td>
</tr>
<tr>
<td>Trace Components 2%</td>
<td>Non-methane volatile organic carbons (NMVOC)</td>
<td>Halocarbons</td>
</tr>
</tbody>
</table>

Figure 1. Biogas composition

A goal of this project is to encourage total resource-recovery on the farm. This idea is generated from the concept of engineering agricultural systems for sustainable development where resources are recycled on the farm reducing the use of off-farm non-renewable resources. Thus, this project addresses this opportunity by investigating ways to process anaerobic digester biogas (ADG), thereby, increasing its utilization. In particular, any system for conversion of biogas to energy either requires a method to remove toxic and corrosive contaminants from biogas, or special procedures to accommodate the deleterious effects of contaminants in the biogas stream. Presently, the internal combustion (IC) engine is the most effective and economically viable energy converter used with ADG. The two most common on-farm approaches are changing oil (IC engines) on a regular basis (numerous operators change oil weekly), or use of Iron Sponge (iron impregnated wood chips) as a filter to remove contaminants (principally hydrogen sulfide, H₂S) from biogas before introduction of biogas into the energy converter. For more futuristic combined heat and power (CHP) systems such as microturbines and fuel cells, the removal of contaminants is as, or more, critical than for the IC engine.

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¹ Source: [http://www.novaenergie.ch/iea-bioenergy-task37/Dokumente/Fisering_4-4.PDF](http://www.novaenergie.ch/iea-bioenergy-task37/Dokumente/Fisering_4-4.PDF)
Specifically the major contaminant is hydrogen sulfide and recent measurements of H₂S concentrations of ADG from six New York farms indicate concentrations ranging from approximately 600 ppm to 6000 ppm. There are numerous chemical, physical and biological methods utilized for removal of H₂S from a gas stream. Many of these methods are labor intensive and generate a waste stream that poses environmental disposal concerns and risks.

SCOPE OF PROJECT

The main objectives were to:

- Evaluate the performance and variability of dairy AD systems through extensive monitoring of biogas composition and documenting its temporal variation.
- Determine and assess the performance of biogas processing systems best suited for farm operations.
- Assess the potential for alternative biogas uses.

This report presents the results from: 1) extensive data acquisition from sampling biogas from dairy AD systems for composition and variations in biogas composition over time, 2) an in-depth study of the potential benefits of effectiveness of using cow-manure compost for removal of H₂S in biogas and 3) an assessment of economics of processing biogas for inclusion in a natural gas pipeline.

BIOGAS CHARACTERIZATION

Two gas chromatographs (GC's) were used to analyze biogas from Dairy Development International (DDI) which is a 30-acre dairy complex and agri-research facility in Cortland County, approximately 26 miles north of Ithaca, NY. DDI has the capacity to house and milk 850 cows. One GC was stationed at DDI for the duration of the project to monitor a steady raw biogas stream. This GC (Daniel Danalyzer 570) was also utilized to take measurements of the inlet and outlet gas for the bioreactors constructed for removal of H₂S at DDI. The system was programmed to take measurements of the raw biogas stream approximately every 3 hours. Although not the only components analyzed, there were 4 readings of significance gathered from each data set: % CH₄, % CO₂, % N₂ (nitrogen), and BTU content. The Daniel GC is equipped with a thermal conductivity detector (TCD), which measures the difference in thermal conductivity of each compound in the carrier gas. The carrier gas chosen in this application was helium.

The second GC, a SRI 6010C, was set up at Cornell University. Equipped with multiple detectors, a TCD and a flame ionization detector/flame photometric detector (FID/FPD), this GC had the capability to analyze a greater number of compounds. A flame ionization detector (FID) was used to detect hydrocarbon peaks in a gas sample whereas the flame photometric detector (FPD) detects sulfur and phosphorus compounds. For the purposes of this study, however, the concentration of sulfur compounds present in the biogas was of greatest interest and therefore the FPD was the key detector. Raw biogas samples were collected in Tedlar® bags and transported to the Cornell Biological and Environmental Engineering (BEE) laboratory for immediate analysis using the SRI Model 6010C gas chromatograph. Each bag was analyzed three times and the average taken and recorded. In cases where two duplicate bags were collected, the average of all GC analyses (i.e. 3 runs from each bag for a total of 6) was the recorded.

RESULTS FROM BIOGAS COLLECTION AND ANALYSIS
Pellerin et al. (1987) report that water-saturated biogas from dairy manure digesters consist primarily of 50-60% methane, 40-50% carbon dioxide, and less than 1% sulfur impurities, of which the majority exists as hydrogen sulfide. The results from the biogas analysis in this project was consistent within these ranges. The following figures summarize the results of all biogas measurements from DDI and H2S monitoring from four additional farms. Figures 2 to 6 represent data collected at DDI. The average concentration of H2S from samples gathered on 13 different occasions between July 2003 and May 2004 was 1984 ppm (less than 0.2%) with a standard deviation of ± 570 ppm. The error bars indicate variation in the actual analytical results. Two duplicate bags were collected for each sampling event and each sample was analyzed three times. The average of these results provided each point on a given date as shown in Figure 2. The average of CH4 measurements was 60.27% (plus or minus approximately 1%) between July and November 2003 (Figure 3) and over the same measurements, the BTU content averaged 612 for the same period (Figure 5). Figure 4 shows an average for CO2 of 38.2%. CO2 is often just estimated as the balance of the biogas when CH4 is known. Figures 6 shows the daily levels of the biogas (CH4, CO2, N2, BTU level) from July to November 2003 at DDI.

Figure 2. Average H2S measured in biogas at DDI, July 2003 – March 2004

Figure 7 illustrates the variation over time and between the five farms for the concentration of H2S in the biogas. This clearly indicates that specific characteristics of digester systems such as environmental conditions, animal feed, water, addition of other organic materials to the digester may influence the concentration of H2S in the biogas generated. Of particular note is that the H2S concentrations at Mattlink (now Ridgeline Farms) is substantially less than the other farms and is potentially attributable to co-digestion with food wastes and manure. Little formal work in this area has been completed, however, “a few dairy farms with anaerobic digesters in the U.S. have tried mixing food wastes with dairy manure for biogas production. Successful results have been reported with increased biogas production and better gas quality” (Scott and Ma, 2004).
Figure 3. Average daily CH₄ measured in biogas at DDI, July–November 2003.

Figure 4. Average daily CO₂ measured in biogas at DDI, July–November 2003.
Figure 5. Average daily BTU content measured in biogas at DDI, July–November 2003.

Figure 6. Raw biogas analysis at DDI, July–November 2003.
Figure 7. Average H$_2$S concentrations at 5 dairy farms in upstate New York, July 2003-Mar. 2004

Figure 8. Daily Average Methane Concentration in Biogas at DDI (July 2003)

It appears that ambient temperatures may have a small effect on CH$_4$ content of biogas at DDI. However, the explanation for the small variations of CH$_4$ content with temperature, whether
due to GC sensitivity to ambient temperature changes or a function in biogas volumetric change as a function of temperature variations is not resolved. Additional graphs depicting the variation in CH₄ content on a daily, weekly and monthly basis are presented in a report to NYSERDA (Scott et al, 2006).

**BIOGAS PROCESSING**

A significant goal of this project has been to consider the potential for biofiltration to reduce (remove) the concentration of H₂S because all energy converters need to operate at H₂S levels significantly less than that found in raw biogas. Zicari (2003) has considered the utilization of cow-manure compost for removal of H₂S from AD biogas using small-scale reactors. Slipstreams of AD biogas (approximately 60% methane, 40% carbon dioxide and 1000-4000 ppm of H₂S) from an operating system at AA Dairy and Dairy Development International (DDI) were passed through reactor sections of a cow manure compost mixture within polyvinyl chloride cylinders of 0.1 m in diameter and 0.5 m in length. The mature cow manure compost (60 days in AA Dairy's outdoor windrow system) was mixed in a 1:1 ratio with dry maple wood chips. Columns have shown over 90% removal efficiency for the early stages of these tests (Figures 9 and 10). The removal efficiency (RE) is defined as the difference in inlet and outlet concentrations of H₂S divided by the inlet concentration.

(Figure 9) continued to operate with RE's above 85% for 33 days before falling off to 55% by day 44. Column A (Figure 10) decreased to 50-60% RE after 16 days and performed at this level for the rest of the run, except for an increase to around 80% RE between days 37-40. Runs were terminated after 44 days, as both columns A and B neared 50% RE, to examine the compost for sulfur accumulation. The H₂S elimination capacity of columns A and B ranged from 24-112 and 16-118 g H₂S/m³ packing/hr, respectively. The total mass of H₂S removed from the gas during these experiments is estimated at 135 and 127 g H₂S, respectively for columns A and B. These values approach a maximum value of 130 g H₂S/m³ packing/hr reported for organic media by Yang and Allen (1994).

![Figure 9. Removal efficiencies (○) and inlet concentrations (■) for Column A.](image-url)
Figure 10. Removal efficiency (○) and inlet concentration (■) for Column B.

Additional studies (Scott et al., 2006) recorded relative maxims in the maximum daily bed temperatures corresponding with maxims in column removal efficiencies followed shortly by reductions in performance. These data, and that for trials in Figures 9 and 10, are suggestive of the existence of a very tight optimum temperature operating range, which, when exceeded, creates biological upset and a subsequent reduction in performance.

ECONOMIC ASSESSMENT OF BIOGAS INJECTION INTO NATURAL GAS PIPELINE

A potential use of biogas, which avoids the large thermodynamic inefficiencies of conversion to electricity, is to use biogas for heating directly. An interesting option is the possibility of introducing biogas into the natural gas pipeline (NGP), given the basic characteristics of biogas as a "low grade" natural gas. Biogas recovery and processing (includes cleaning and upgrading) for injection into the natural gas pipeline depends on the financial viability of the project, which is determined from the point of view of the investor. Investors may include the farmer, local, state, and federal government agencies as well as research and development companies.

The main limitations to upgrading biogas to natural gas quality are not technical, but economical and political. The willingness of a buyer to purchase the upgraded biogas is crucial and a buyer must be established during the initial stages of the project. A minimum price that the buyer will pay for the biogas during the lifetime of the project also must be established.

The cost of upgrading biogas varies considerably and very few 'hard numbers' are available in the literature. From a literature review, the limited data that are available pertain mainly to upgrading landfill gas (LFG) and demonstrates that currently, processing biogas to natural gas is likely to be feasible only for large biogas producers with substantial gas recovery. Since LFG is similar to the biogas produced as a result of AD of manure on a dairy farm, much of the
economic information from LFG processing projects can be useful for application to dairy biogas processing project.

It is assumed that the AD biogas from a dairy has the following parameters:

\[ CH_4 = 60\%, \ CO_2 = 38\%, \ N_2 \text{ and } O_2 \text{ Combined } = 2\%, \ H_2S = 3,000 \text{ ppm,} \]

and that the minimum gas quality standards for injection into the natural gas pipeline are:

\[ CH_4 = 97\%, \ CO_2 = 2\%, \ N_2 \text{ and } O_2 \text{ Combined } = 1\%, \ H_2S < 4\text{ppm.} \]

**PRESENT WORTH ANALYSIS**

In order to determine if a biogas upgrading is economically viable on dairy farms of various sizes, present worth analyses were conducted (Saikkonen, 2006; Scott, et al., 2006). In order to determine the present worth (PW) of upgraded dairy biogas sales, several factors or parameters were taken into considerations. They include: (a) number of cows on the dairy farm, (b) selling price of the processed dairy biogas, (c) interest rate and (d) connection to the pipeline including various pipeline lengths.

For the purpose of this analysis, five different size dairies (500, 1000, 3000, 5000 and 10000 milking cows) were considered. According to the U.S. Energy Information Administration, wellhead natural gas prices have ranged from $2.00/million BTU (MBtu) to over $14.00/MBtu in the past five years (U.S. Energy Information Administration, 2005). In the fall of 2005, wellhead prices of up to $11.00/MBtu were observed. As of December, 2005 wellhead natural gas prices were as high as $14.85/MBtu (The Kiplinger Letter, 2005). Based on this information, selling prices of $2.00, $4.00, $6.00, $8.00, $10.00 $12.00 and $14.00 per MBtu were considered for this analysis. Interest rates of 3%, 5% and 7% were used.

Figures 11 -14 illustrate the present worth of biogas sales based on processed biogas selling price, pipeline installation and interest rates. For a 500-cow dairy, the graphs show that a profit begins being made if the processed biogas is sold for $12.00/MBtu, assuming that no additional pipeline is installed and that the interest rate is low (3%). A profit can be made if pipeline is installed (up to ½ mile), as long as the processed biogas sells for at least $14.00/MBtu.

For a 1,000 cow dairy, the data shows that a profit will not be made unless the upgraded biogas is sold for at least $6.00/MBtu, assuming a low interest rate of 3%. If the upgraded biogas is sold for less than $6.00/MBtu, regardless of the amount of pipeline installed or interest rate over the lifetime of the project, money will be lost. If the biogas is sold for $8.00/MBtu, a profit is made as long as the pipeline installation is not over ½ mile long. At a selling price of $10.00/MBtu, a profit may be made even if up to 1 mile of pipeline is installed and at a higher interest rate.

For a 3,000 cow dairy, a profit begins being made if the upgraded biogas is sold for at least $4.00/MBtu, provided that no pipeline is installed and that the interest rate is low (3%). If it is necessary to install pipeline to connect to the natural gas network, the gas must be sold for at least $6.00/MBtu. With a dairy of this size, if a pipeline of up to one mile must be installed, a profit can still be made, even at a high interest rate (7%), as long as the processed gas is sold for $6.00/MBtu or more.

As with the 3,000 cow dairy, a profit can be made on a 5,000 cow dairy if the processed gas is sold for at least $4.00/MBtu, provided that no pipeline installation is necessary and that the interest rate is relatively low. If the processed biogas seller receives at least $6.00/MBtu for the gas, and installs ½ mile or less of pipeline, significant revenue can be made over the 10 year life
of the project. For example, if the seller installs \( \frac{1}{2} \) mile pipeline, at 3% interest, over $1,000,000 in revenue will be made.

Extrapolating the data, the "break even" price that the processed biogas must sell for on a 10,000 cow is $3.50/MBtu. If the gas is sold for at least $4.00/MBtu, with no pipeline installation and a low interest rate (3%), over $1,000,000 in profit can be made over the course of the project. If the gas is sold at a higher rate ($8.00 - $10.00 per MBtu), a significant profit of approximately $3,832,736 and $5,909,250 can be made, respectively, even if up to one mile of pipeline must be installed and at a high interest rate (7%).

Figure 11. Farm Size and Profitability without pipeline installation, 5% interest
Figure 12. Farm Size and Profitability with ¼ mile pipeline installation, 5% interest.

Figure 13. Farm Size and Profitability with ½ mile pipeline installation, 5% interest.

Figure 14. Farm Size and Profitability with 1 mile pipeline installation, 5% interest.
Conclusion

Measurements of biogas from five New York farms and detailed measurements at Dairy Development International (DDI) provide information about composition and quantity of constituents in biogas over time (day, week and year). Methane (CH₄) content at DDI, measured over months, averaged 60.3% ± 1% with an average BTU content of 612 ± 11 BTU. Similarly, carbon dioxide (CO₂) and Nitrogen (N₂) averaged 38.2 % and 1.5% respectively. Hydrogen sulfide (H₂S) concentrations at DDI averaged 1984 ppm with a standard deviation of ± 570 ppm over the period of almost a year. Measurements of H₂S at five NY farms illustrated a rather wide variation in H₂S concentrations from about 600 ppm to over 7000 ppm. It is suggested that the lower concentration of H₂S appears to be due to addition of food wastes to the AD and the higher sulfur concentration of the farm water supply may be the reason for the much higher H₂S concentrations at the one NY farm. For those digesters not adding food waste and not having high concentrations of sulfur in the water, the H₂S concentrations appear to range from about 1500 ppm to 4000ppm. Daily variations in CH₄ were measured and appeared to correlate with ambient temperatures but whether these small daily variations of about ± 0.5% were due to temperature sensitivity of the gas chromatograph or a real CH₄ concentration variation was not determined. These results agree with the often quoted generalized concentrations of 60% CH₄, 40% CO₂ and 600 BTUs for dairy-derived biogas.

Cow-manure compost for removal of H₂S from AD biogas was used in small-scale reactors. The total mass of H₂S removed from the gas during these experiments was estimated at 127 and 135 g H₂S. These values approach a maximum value of 130 g H₂S/m³ packing/hr reported in the literature for organic media. Correlation of bed temperature data with removal efficiency (RE) is suggestive of the existence of a very tight optimum temperature operating range, which, when exceeded, creates biological upset and a subsequent reduction in performance (reduced RE).

A technical and economic assessment of processing of biogas for injection to the natural gas pipeline, while dependent on parameters of biogas quantity, price for processed biogas, proximity of the biogas producer to the natural gas pipeline and the interest rate, suggests that a real possibility exists for injecting biogas to the natural gas pipeline dependent, of course, on the values of the parameters indicated. The results of the economic analysis showed that for all farm sizes studied (500, 1000, 3000, 5000 and 10000) a profit from injecting biogas to a natural gas pipeline is possible depending on primarily the biogas selling price and the proximity to the natural gas pipeline. An innovative demonstration project for upgrading biogas to natural gas pipeline should be considered because upgrading dairy biogas to natural gas quality has not been done in the US.

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References


