EERC®
Energy & Environmental Research Center
UNIVERSITY OF NORTH DAKOTA
15 North 23rd Street — Stop 9018 / Grand Forks, ND 58202-9018 / Phone: (701) 777-5000 Fax: 777-5181
Web Site: www.undeerc.org

April 30, 2009

Mr. Timothy Edman
Manager, Regulatory Administration
Xcel Energy, Inc.
414 Nicollet Mall
Minneapolis, MN 55401

Dear Mr. Edman:

Subject: Quarterly Progress Report Entitled "Mitigation of Hydrogen Sulfide with Concomitant Enhancement of Microbial Methane Production in Biomass Digesters"
Contract No. RD3-68; EERC Fund No. 9967

Enclosed please find the subject report. If you have any questions, please contact me by phone at (701) 777-5247 or by e-mail at dstepan@undeerc.org.

Sincerely,

Daniel J. Stepan

Daniel J. Stepan
Senior Research Manager

DJS/cs

Enclosure

Energy & Environmental Research Center, University of North Dakota
15 North 23rd Street, Stop 9018, Grand Forks, ND 58202-9018

Project Title: Mitigation of Hydrogen Sulfide with Concomitant Enhancement of Microbial Methane Production in Biomass Digesters

Contract Number: RD3-68 Milestone Number: 1 Report Date: April 7, 2009

Principal Investigator: Daniel Stepan Contract Contact: Tobe Larson

Phone: (701) 777-5247 Phone: (701) 777-5271

Congressional District: Not Applicable

Congressional District: Not Applicable

# MILESTONE REPORT

Executive Summary: The overall goal of this Energy & Environmental Research Center (EERC) project is to test and demonstrate a novel biotechnology to convert biomass into a biogas having increased methane content and significantly reduced hydrogen sulfide. The project will be conducted at both the bench- and pilot-scale. Laboratory screening tests will establish baseline operating conditions prior to bench- and pilot-scale testing. The EERC has teamed with Haubenschild Farm Dairy, Inc. (HFD), Princeton, Minnesota, to conduct the project.

During this reporting period, key milestones included 1) obtaining agreements with HFD for use of the site, manure, and operating data from the existing digester; 2) obtaining any necessary permits to conduct the research; 3) providing a list of alternative dairies in the unlikely event that manure at HFD is determined unusable or unavailable; 4) ordering equipment and supplies necessary for laboratory screening experiments; 5) conducting equipment quality assurance/quality control (QA/QC) and documenting results; and 6) performing a site visit to collect manure samples for laboratory screening experiments. Project funding provided by customers of Xcel Energy through a grant from the Renewable Development Fund.

Technical Progress:

## Agreement

An agreement has be made between the EERC and HFD to allow the EERC use of the site near Princeton, Minnesota; fresh manure; data from the currently used digester; and other necessary services required to successfully carry out the laboratory- and bench-scale experiments and to operate the pilot-scale digester at HFD. A copy of the agreement letter is included in Appendix A.

## Permits

Laboratory screening tests and bench-scale digester operations will be conducted in the laboratories of the EERC. Testing will be conducted in a manner consistent with policies of the University of North Dakota. No additional permits will be required for testing conducted at the EERC laboratories. The EERC pilot-scale digester will be sited adjacent to HFD's full-scale, 20,000-gpd anaerobic digester. Approximately 60 gpd of fresh manure from the full-scale digester influent manure pipe will be routed to the EERC digester. The effluent from the pilot-scale digester will be directed to HFD's digested manure storage lagoon. Operation of the EERC digester will be conducted in a manner consistent with HFD's existing feedlot permit, and no additional permitting will be necessary.

Alternative Dairies

There are thousands of operating dairies in Minnesota, four of which were identified as having operational anaerobic digesters. Two of those dairies were contacted as potential alternatives in the unlikely event that the manure at HFD is either unusable or unavailable. The following are addresses and contact information for the alternative dairies.

Jerry and Linda Jennissen
Jer-Lindy Farms
31535 463rd Avenue
Brooten, MN 56316
(320) 346-2292

Gary Fehr
Riverview Dairy
26402 470th Avenue
Morris, MN 56267-5370
(320) 392-5609

Ordering of Equipment and Supplies

An Agilent Model 7890 gas chromatograph (GC) with a flame photometric detector (FPD) and a thermal conductivity detector (TCD) was ordered, received, put into operation, and calibrated. Xcel project funds provided approximately one-third of the total cost of the GC system. Two GC columns were also purchased for the project. One of the columns was a GS-GasPro 30 m × 0.32 mm capillary column that is connected to the FPD of the 7890 GC for $H_2S$ analysis. The GS-GasPro column has excellent separation capability to allow elution of volatile sulfur compounds away from large hydrocarbon peaks. This allows for accurate determination of volatile sulfur compounds, such as $H_2S$ and mercaptans, that are commonly present in biogas. The GS-GasPro column also provides the most inert stationary-phase surface for reactive sulfur compounds such as $H_2S$ and mercaptans.

In addition to the GC column, other GC supplies were purchased, including $H_2S$, $CH_4$, and $CO_2$ gas standards; GC operating gas (such as high purity $N_2$) and gas purifiers; gas regulators; GC septa; gas sampling bags; and air-tight syringes and replacement needles as well as some other consumables, such as experimental glassware and Teflon-lined butyl stoppers, in preparation for laboratory screening experiments.

Equipment QA/QC Documentation

Since the purpose of this project is mitigation of $H_2S$ with concomitant enhancement of $CH_4$ production, it is of critical importance that gas analyses be accurate and precise. There are many analytical methodologies that can be used to quantify $H_2S$, $CH_4$, and $CO_2$. Based on the EERC's previous research experience and published literature, gas chromatography was selected as the preferred method to analyze $H_2S$, $CH_4$, and $CO_2$ in dairy manure biogas samples. An existing EERC-owned Agilent 6890N GC system, equipped with a TCD and a flame ionization detector (FID), will be used for $CH_4$ and $CO_2$ analyses, which are expected to be up to around 70% and 50%, respectively. The TCD is a universal detector and is also capable of detecting $H_2S$; however, its sensitivity to $H_2S$ is low, and therefore, the TCD is not suitable for this project.

*Agilent 6890N GC/TCD Operating Parameters*

| | |
|---|---|
| Column Type | Haysep DB 100/120; Altech, Deerfield, Illinois |
| Length and i.d. (inside diameter) | 30’ x 1/8” × 0.85” SS |
| Carrier Gas | Helium 25 mL/min |
| | |
| Oven | |
| Initial Temperature | 140°C, 6 min |
| Ramp | 50°C/min to 175°C and hold |
| | |
| Inlet | |
| Initial Temperature | 143 |
| Flow | Helium 26 mL/min °C |
| | |
| Detector | TCD |
| Temperature | 200°C |
| Reference Flow | 40 mL/min |
| | |
| Column Compensation | Derive from front detector |

The analysis of $H_2S$ at both high and low concentrations is critical, since $H_2S$ mitigation is a focus subject of this project. $H_2S$ concentration is expected to be as high as 3000–5000 ppmv in the untreated digester samples and as low as 0–50 ppmv in the digester samples treated with the EERC’s additive. An Agilent 7890A GC with a FPD and a TCD will be used for $H_2S$ analysis. The FPD will selectively detect sulfur compounds, including $H_2S$.

*Agilent 7890A GC/FPD Operating Parameters*

| | |
|---|---|
| Column Type | GS-GasPro, J&W Scientific, Folsom, California |
| Length and i.d. | 30 m × 0.32 mm |
| Carrier Gas | Helium 4 mL/min |
| | |
| Oven | |
| Initial Temperature | 35°C |
| Ramp | 15°C/min to 65°C |
| | 40°C/min to 200°C |
| Inlet | |
| Initial Temperature | 65°C |
| Flow | Helium 26 mL/min |
| | |
| Detector | FPD |
| Temperature | 220°C |
| $H_2$ | 50.0 mL/min |
| Air | 60 mL/min |
| $N_2$ Makeup | 50 mL/min |

In order to satisfy the required analytical QA/QC commitments for this project, resolution, quenching, initial calibration curves, detection limitation, precision, and accuracy for these instruments were determined using gas standards purchased from Praxair; Matheson Tri-Gas, Inc.; and Airgas Co. Calibration curves show the relationship between chromatogram peak intensity and compound concentration. Determination of initial accuracy depicts the degree of closeness that measurements are to the actual values in certified reference gases. Determination of instrument precision illustrates the ability of replicate analyses to deliver similar results. Finally, resolution and quenching issues, which affect the overall quality of the tests, were determined. Resolution shows the ability of a particular instrument and chromatographic column to separate and quantify two or more compounds, while quenching is the inability to effectively do so.

The QA/QC efforts have confirmed that analysis of anaerobic digester biogas from dairy manure for $CH_4$, $CO_2$, and $H_2S$ at the concentrations expected will be resolvable, precise, and accurate.

*$CH_4$ and $CO_2$ Analysis Using Gas Standards*

- Resolution and Calibration

$CH_4$ and $CO_2$ are well-separated and resolved on this column from air ($N_2$ and $O_2$; Figure 1). Linear calibration curves for $CH_4$ and $CO_2$ are plotted in Figures 2 and 3, respectively. The large $R^2$ values, greater than 0.99, indicate a very high correlation between the gas concentration and the peak area.

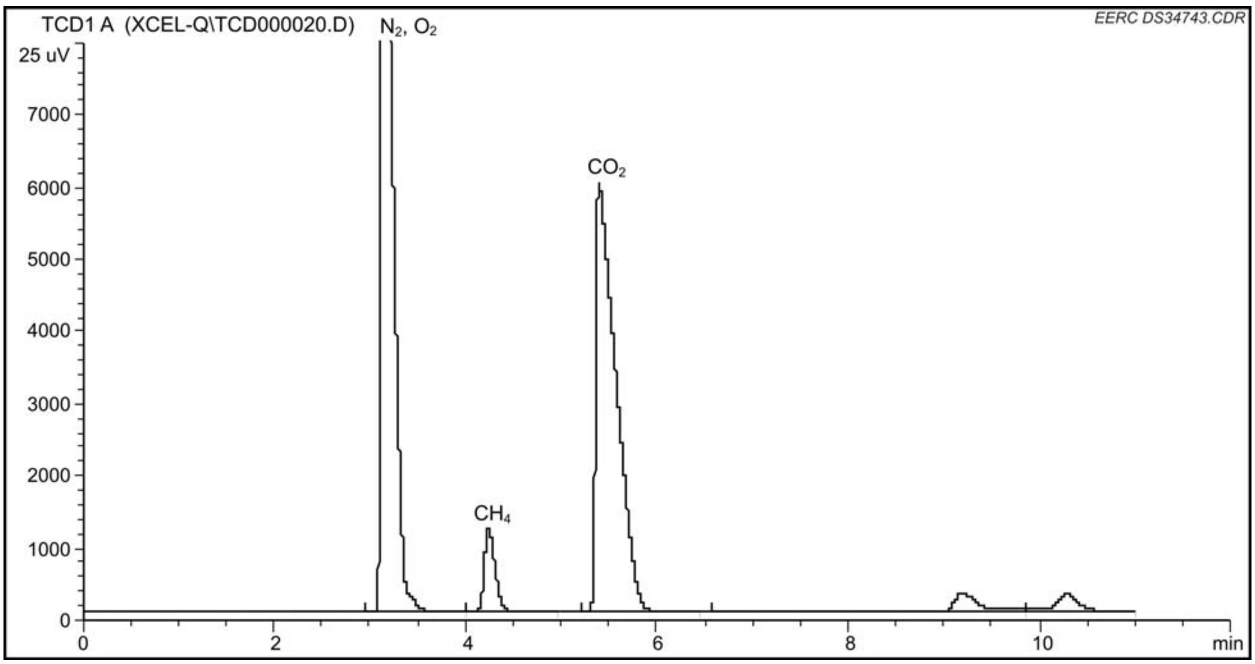


Figure 1. Agilent 6890N GC chromatogram of $CH_4$ and $CO_2$ in standard gas mixture.

Precision was determined by calculating the relative error of the peak area between duplicate injections. Duplicate injections of a $CH_4$ (4.95%) and $CO_2$ (4.94%) gas standard was conducted to determine the precision of $CH_4$ and $CO_2$ analyses. Results are shown in Tables 1 and 2.

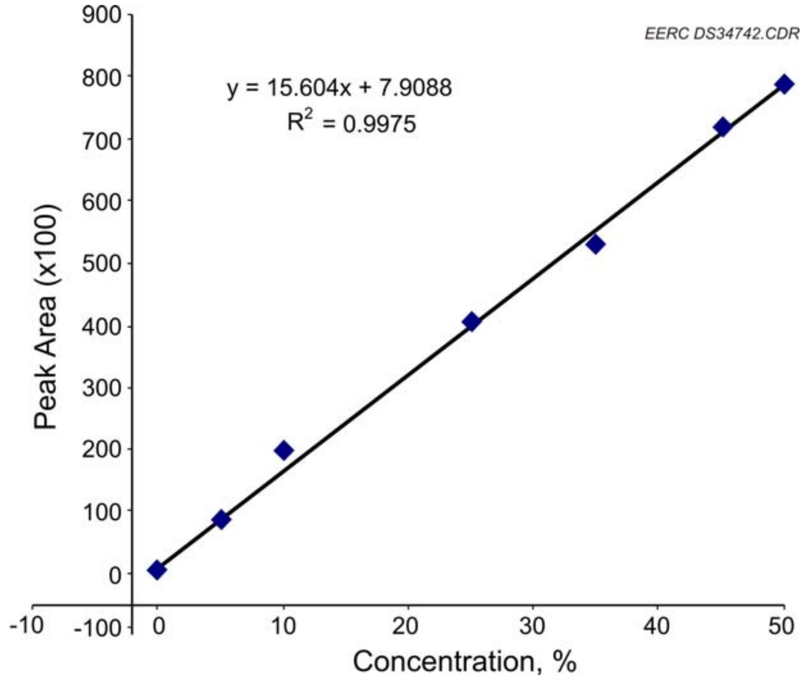


Figure 2. Calibration curve for $CH_4$ in a standard gas mixture – Agilent 6890N GC/TCD.

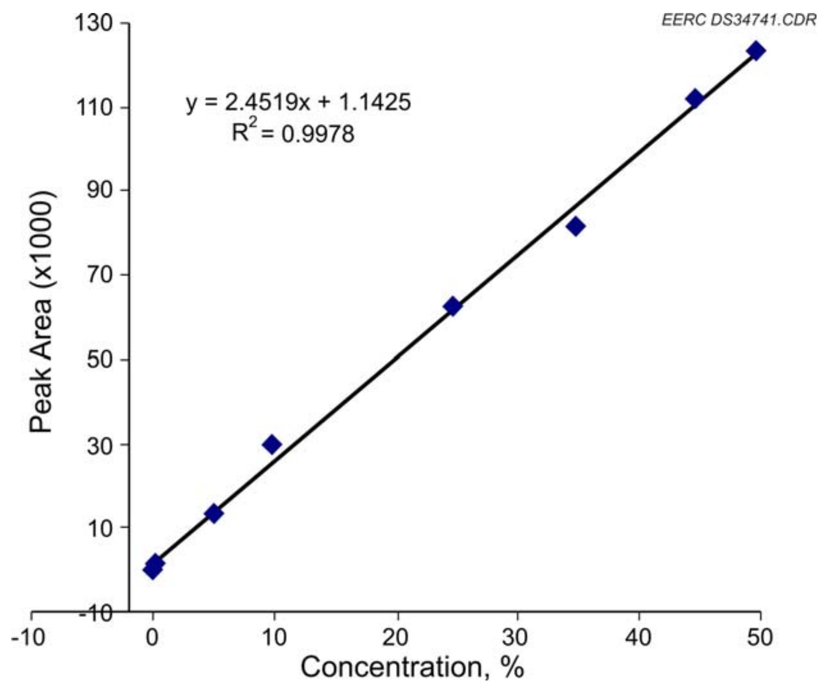


Figure 3. Calibration curve for $CO_2$ in a standard gas mixture – Agilent 6890N GC/TCD.

**Table 1. Precision of $CH_4$ Analysis**

| | Peak Area |
|---|---|
| 1st Injection | 8498 |
| 2nd Injection | 8642 |
| Average | 8570 |
| St. Dev.* | 102 |
| Relative Error** | 1.2% |

* Standard deviation.
** Relative error: (st. dev./average) × 100%.

**Table 2. Precision of $CO_2$ Analysis**

| | Peak Area |
|---|---|
| 1st Injection | 13605 |
| 2nd Injection | 13436 |
| Average | 13520 |
| Std. Dev. | 119 |
| Relative Error | 0.9% |

- Accuracy

Accuracy was determined by analyzing reference gases of known concentration to determine the ability of the instrument, as configured, to determine the concentration of $CH_4$ and $CO_2$. Standard curves for $CH_4$, $CO_2$, and $H_2S$ were made using a gas mixture containing 49.5% $CO_2$, 0.5% $H_2S$, and balanced by $CH_4$. The gas mixture was provided by Praxair Distribution, Inc., Geismaar, Louisiana. The reference gases of $CH_4$ and $CO_2$ used for the accuracy tests were purchased from Matheson Tri-Gas Inc., Twisburg, Ohio. Accuracies of $CH_4$ and $CO_2$ analyses are listed in Tables 3 and 4, respectively.

**Table 3. Accuracy of $CH_4$ Analysis**

| Concentration of the Reference | Analytical Result | Relative Error |
|---|---|---|
| 99.0% | 97.5% | −1.5% |
| 9.9% | 9.8% | −0.5% |

**Table 4. Accuracy of $CO_2$ Analysis**

| Concentration of the Reference | Analytical Result | Relative Error |
|---|---|---|
| 99.8% | 100.4% | 0.6% |
| 9.98% | 9.96% | −0.2% |

- Detection limits (GC/TCD)

Under our GC operation conditions, the detection limits of GC/TCD on $CH_4$ and $CO_2$ are 2.2 and 0.8 ppmv, respectively.

*$CH_4$ and $CO_2$ Analysis on Biogas from Anaerobic Digestion of Dairy Manure*

- Resolution of the dairy manure biogas components by GC/TCD

Figure 4 is the GC/TCD chromatogram of the biogas produced from dairy manure. The manure was incubated in a 160-mL serum bottle capped with a butyl stopper and aluminum seal and was incubated at 30°C for 24 days. $CH_4$ and $CO_2$ were well-separated and not interfered by any other components in the biogas.

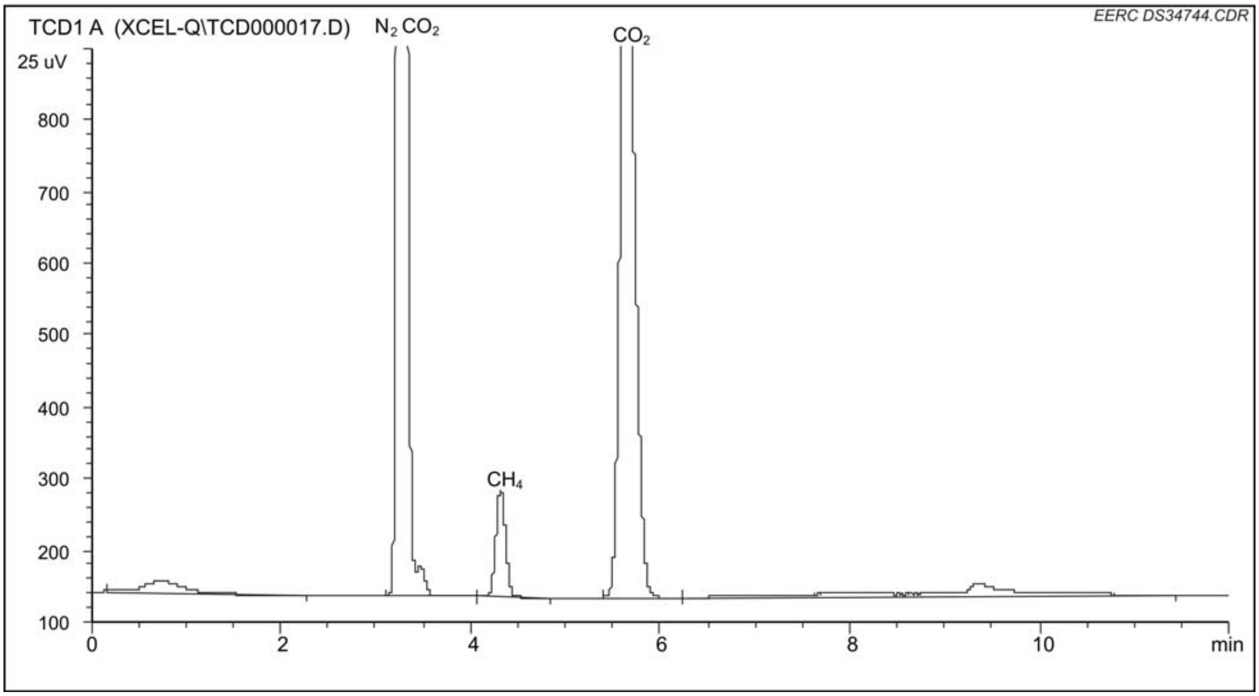


Figure 4. Agilent 6890N GC/TCD chromatogram of biogas from the anaerobic digestion of dairy manure.

- Precision of the analysis of $CH_4$ and $CO_2$ from biogas produced from dairy manure

Results of duplicate injection are listed in Table 5. The relative errors on $CH_4$ and $CO_2$ were small, 1.2% and 1.7%, respectively.

**Table 5. Precision of $CH_4$ and $CO_2$ Analysis on the Manure Sample**

| | $CH_4$ (Peak Area) | $CO_2$ (Peak Area) |
|---|---|---|
| 1st | 8591 | 88092 |
| 2nd | 8740 | 85941 |
| Average | 8665.5 | 87016.5 |
| St. Dev. | 105.359 | 1520.359 |
| Relative Error | 1.2% | 1.7% |

*$H_2S$ Analysis Using Gas Standards*

- Calibration

The FPD response to $H_2S$ concentration is nonlinear. Sulfur response is determined by a square root relationship since the flame reaction converts sulfur atoms to an $S_2$ complex. Therefore, the calibration curves of sulfur-compounds on FPD are usually plotted logarithmically. The response of $H_2S$ to the FPD is logarithmic as shown in Figure 5. The large $R^2$ value indicates a very high log-log correlation between the gas concentration and the peak area.

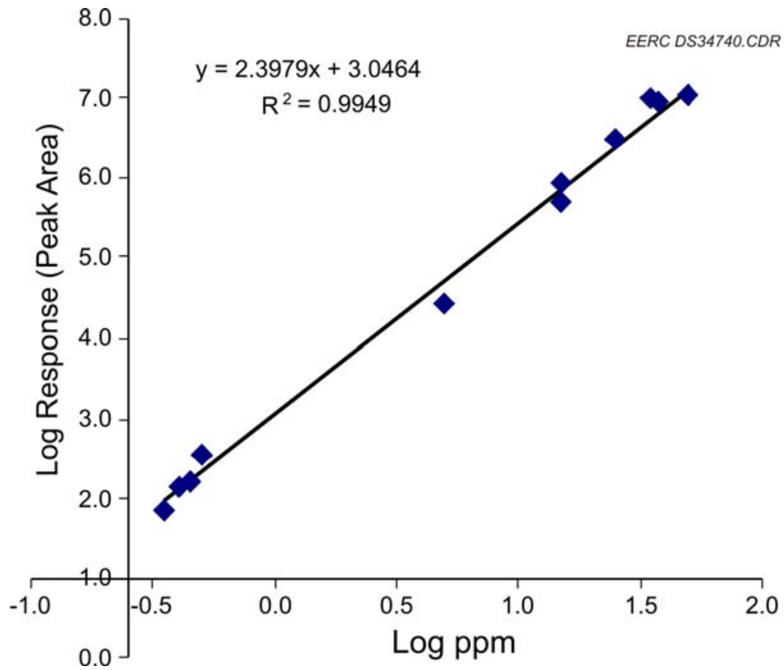


Figure 5. Calibration curve for $H_2S$ by Agilent 7890A GC/FPD).

- Precision

Precision was determined by calculating the relative error of the peak area between duplicate injections. Duplicate injection of a 50 ppmv $H_2S$ standard was conducted to determine the precision of $H_2S$ analysis, and the results are listed in Table 6. The low relative error indicates that replicate analyses will give very similar results.

**Table 6. Precision of $H_2S$ Analysis**

| | Peak Area |
|---|---|
| 1st Injection | 10,833,900 |
| 2nd Injection | 10,618,400 |
| Average | 10,726,150 |
| St. Dev. | 152,382 |
| Relative Error | 1.4% |

- Accuracy

Accuracy was determined by quantitate $H_2S$ in a reference gas mixture from another lab at the EERC. This gas mixture contained 5000 ppmv $H_2S$, and the gas mixture was purchased from Airgas Co., Radnor, Pennsylvania. The gas was then diluted to 30 ppmv and 2 ppmv for the accuracy test. The analytical results are listed in Table 7. The results are very close in value to the standard concentrations.

**Table 7. Accuracy of $H_2S$ Analysis**

| Samples of Known Concentrations | EERC Analytical Results | Relative Error |
|---|---|---|
| 2 ppmv | 1.94 ppmv | −3.0% |
| 30 ppmv | 29.1 ppmv | −2.9% |

- Detection limit

Under the EERC's GC operating conditions, the detection limit of the GC/FPD on $H_2S$ is 100 ppbv.

- Quenching

Despite the fact that FPD is a selective detector to sulfur compounds, hydrocarbons at certain concentrations may also give a signal on the FPD. Coeluting of hydrocarbons with the target sulfur compounds may cause drastic quenching or superimposition of eluting compounds. By careful selection of a suitable GC column and optimization of operating parameters (oven temperature program, flow rate, etc.), no quenching effect on $H_2S$ was observed. Figure 6 shows dairy manure biogas chromatograms obtained by use of a flow splitter dividing the eluted sample to two detectors, an FPD and TCD. The upper panel shows $H_2S$ detected by FPD, the lower panel shows the biogas components ($N_2$, $O_2$, $CH_4$, $CO_2$, et al.) not resolved under these operating conditions) detected by TCD. The upper panel of Figure 6 shows the $H_2S$ peak on FPD, while the lower panel shows any signals on TCD.

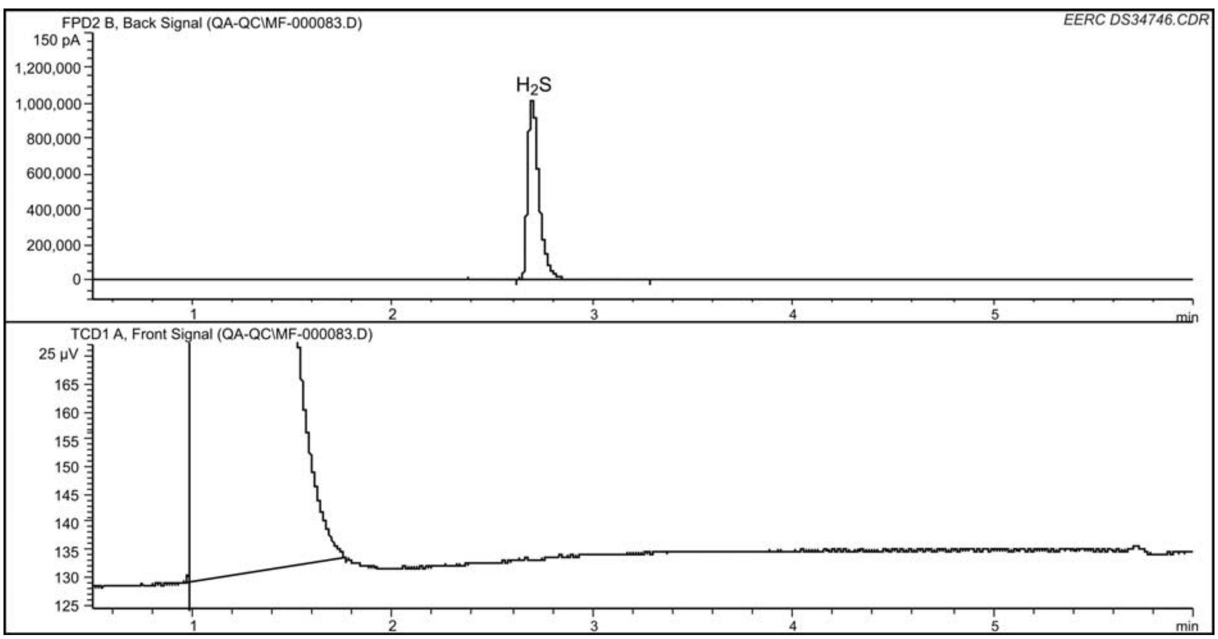


Figure 6. Agilent 7890A GC/FPD and TCD chromatograms of the biogas from anaerobic digestion of the manure sample.

The big peak shown on the TCD detector consisted of $N_2$, $O_2$, $CH_4$, $CO_2$ and, perhaps, some other light hydrocarbons. As can be seen from the baseline of the TCD chromatogram (the lower panel), no peak eluted at the retention time close to $H_2S$. This confirms that no quenching occurred under these analytical conditions. This column (GS-GasPro) was then installed on the EERC's 6890 GC with FID, and the same GC operating conditions were adopted; once again, no peak was eluted at this $H_2S$ retention time, confirming that no quenching occurred under our analytical conditions.

- Precision of $H_2S$ analysis on the biogas

A test on precision of $H_2S$ on the dairy manure biogas was conducted. Results of duplicate injections are listed in Table 8.

**Table 8. Precision of $H_2S$ analysis on the Manure Sample**

| | Peak Area |
|---|---|
| 1st Injection | 114,131 |
| 2nd Injection | 120,071 |
| Average | 117,101 |
| St. Dev. | 4,200 |
| Relative Error | 3.6% |

Haubenschild Farm Dairy Site Visit and Manure Collection

EERC personnel visited the HFD in March 2009 to tour the farm and observe the operation of the anaerobic digester and biogas-powered combined heat and power system. A tentative location for siting the EERC pilot-scale digester was established, and preliminary plans for connecting to the existing system were developed.

Four 5-gallon pails of fresh manure were collected from the manure pit for preliminary characterization and laboratory screening experiments. An aliquot of the digester influent manure was analyzed at the Minnesota Valley Testing Laboratories (New Ulm, Minnesota) for solids content and chemical oxygen demand (COD). Results of these analyses are listed in Table 9. The fresh manure had a relatively high total solids content, 11.1%, compared to other dairies the EERC has visited, where total solids have been only 5% to 8%. A significant portion of the organic content, as measured by COD, is in the liquid portion of the manure. Soluble COD was measured to be 61,400 mg/L, compared to a total COD of 96,000 mg/L.

**Table 9. Haubenschild Farm Dairy Digester Influent Manure Analysis**

| Parameter | As-Received |
|---|---|
| Total Solids (TS), % | 11.1 |
| Total Volatile Solids, % of TS | 80.0 |
| Total Suspended Solids, mg/L | 33,200 |
| Total Volatile Suspended Solids, mg/L | 15,000 |
| Total COD, % | 9.60 |
| Soluble COD, mg/L | 61,400 |

**Uncited References**

Beiner, K., and Popp, P, 2006, Sulfur compounds, *in* Leo, M. et al. (eds), Chromatographic analysis of the environment: New York, CRC Press, Edition 3, p. 343–367.

Ellis, J., Vickers, A.K., and George, C., 2002, Capillary column selectivity and inertness for sulfur gas analysis in light hydrocarbon streams by gas chromatography, Agilent Technologies, Fuel Chemistry Division Preprints, v.47, no. 2, p. 703. www.anl.gov/PCS/acsfuel/preprint%20archive/Files/47_2_Boston_10-02_0196.pdf (accessed March 2009).

Kalontarov, L., Jing, H., Amirav, A., and Cheskis, S., 1995. Mechanism of sulfur emission quenching in flame photometric detectors: Journal of Chromatography A, v. 696, p. 245–256.

Konieczka, P., and Namiesnik, J., 2009, Quality assurance and quality control in the analytical chemical laboratory, a practical approach: Boca Raton, Florida, CRC Press.

Lindqvist, L., 2005, Sulfur-specific detection in air by photoionization in a multiple detector gas chromatographic system: Journal of High Resolution Chromatography, v. 12, p. 628–631.

Olesik, S.V., Pekay, L.A., and Paliwoda, E.A., 1989, Characterization and optimization of flame photometric detection in supercritical fluid chromatograph: Anal. Chem., v. 61, p. 58–65.

Pandey, S.K., and Kim, K.H., 2009, Comparison of different calibration approaches in the application of thermal desorption technique: a test on gaseous reduced sulfur compounds: Microchemical Journal, v. 91, p. 40–46.

Pandey, S.K., and Kim, K.H., 2008, The fundamental properties of the direct injection method in the analysis of gaseous reduced sulfur by gas chromatography with a pulsed flame photometric detector: Analytica Chimica Acta, v. 615, p. 165–173.

Additional Milestones: None.

Project Status: The project is on schedule and within budget. The key milestone for the upcoming quarter will be the initiation of laboratory screening experiments to assess additive formulations. Though not an identified milestone, EERC staff will also establish an anaerobic seed reactor that will be used to establish a culture of bacteria that can be used in both laboratory screening experiments and bench-scale test trials.

# APPENDIX A

# HAUBENSCHILD FARMS’AGREEMENT LETTER

RECEIVED

MAR 24 2009

EERC CONTRACTS

Mr. Dan Stepan
Senior Research Manager
University of North Dakota
Energy & Environmental Research Center
15 North 23rd Street, Stop 9018
Grand Forks, ND 58202-9018

Dear Mr. Stepan:

This letter is to reaffirm Haubenschild Farms' participation in the research project you were awarded by Xcel Energy's Renewable Development Fund, Third Funding Cycle, entitled "Mitigation of Hydrogen Sulfide with Concomitant Enhancement of Microbial Methane Production." This letter also serves as an agreement for the Energy & Environmental Research Center (EERC) to site a pilot-scale digester at Haubenschild Farm Dairy to conduct the research.

Haubenschild Farm Dairy agrees that:

- Haubenschild will provide a location to site the pilot-scale biodigester and manure to be used as a feedstock.
- Haubenschild will provide the EERC with access to electricity to run its equipment.
- The EERC will reimburse Haubenschild for electricity usage.
- Haubenschild will allow the EERC to make necessary plumbing connections to feed manure from the Haubenschild's system to the EERC's pilot-scale reactor. Digester effluent, estimated to be 60 gallons per day, from the EERC pilot-scale digester can be routed to Haubenschild's existing manure storage pond.
- Operation and performance data from the existing on-farm digester will be made available to the EERC for use in designing the bench- and pilot-scale digesters.
- For the purposes of comparison, the EERC will be allowed to analyze the biogas quality from Haubenschild's existing digester.
- Biogas from the EERC digester will be made available to Haubenschild.
- The EERC will provide all labor necessary to operate its pilot-scale system.
- Haubenschild and the EERC will each be responsible for their own employees while acting within the scope of their employment.
- At the conclusion of testing, the EERC will be responsible for the removal of its equipment and for restoring the site to pretest conditions.
- Haubenschild agrees that the technology being developed in the demonstration is the sole property of the EERC, and Haubenschild will not claim or disclose information about the technology or allow others access to the equipment without written consent of the EERC.


Reduction of hydrogen sulfide in digester biogas is a very important area of research for biogas production. Scrubbing hydrogen sulfide from digester biogas is difficult and costly. Significant reduction of hydrogen sulfide, while simultaneously producing more methane, would be a most welcome technological advance. It will promote more extensive implementation of anaerobic digestion of biomass resources for electrical energy production, especially with the high-efficiency fuel cell technology.

We look forward to working with you on this exciting new technology.

Sincerely,

Dennis Haubenschild