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

July 29, 2010

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 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
Senior Research Manager

DJS/kmd

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: 6 Report Date: July 29, 2010

Principal Investigator: Daniel J. Stepan Contract Contact: Tobe M. Larson

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

Congressional District: Not Applicable

Congressional District: Not Applicable

MILESTONE REPORT

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 with increased methane content and significantly reduced hydrogen sulfide. The project is being conducted at both the bench and pilot scale. Laboratory screening tests have established baseline operating conditions. The EERC has teamed with Haubenschild Farm Dairy, Inc., Princeton, Minnesota, to conduct the project.

During this reporting period, key milestones included the completion of bench-scale experiments using Riverview Dairy manure to compare process performance of control and experimental plug flow anaerobic digesters, as well as limited operation using Haubenschild Farm Dairy manure. Batch serum bottle experiments were also conducted to determine an appropriate dose for use with Haubenschild Dairy manure samples. The serum bottle tests showed that a combination of additive plus a scavenger provided a significant benefit to both reducing sulfide in the headspace biogas and increasing methane content. The results from operation of the bench-scale digesters showed good results, with biogas having increased methane production and significant sulfide reduction with the additive treatment of Riverview Dairy manure. Design and fabrication of the pilot anaerobic digester system was also conducted. The pilot system is a 2-ft-diameter, 20-ft-long vessel with a nominal operating volume of 235 gallons. A project progress report was presented to Xcel Energy representatives during their visit to the EERC in June 2010.

The work planned for the next reporting period includes installation and operation of the pilot-scale digester at Haubenschild Farm Dairy and additional serum bottle studies on the combined use of additive and scavenger using representative Haubenschild Farm Dairy manure samples.

Project funding was provided by customers of Xcel Energy through a grant from the Renewable Development Fund.

Technical Progress:

During this reporting period, Haubenschild Farm Dairy removed the manure and remaining gypsum from their anaerobic digester and installed a new cover. Operation of the full-scale digester began in May, and the dairy is presently producing a combustible biogas. Both laboratory screening experiments and bench-scale test trials were conducted with available Haubenschild manure samples. Neither of the samples that were available were necessarily representative of normal operation but rather manure blends that were used in the acclimation and development of adapted methanogenic cultures in the full-scale farm digester.

Laboratory Screening Experiments

Additional laboratory screening experiments were conducted during this reporting period using Haubenschild Farm Dairy manure. Samples were prepared in an anaerobic glove box as described in the Milestone 2 quarterly report. All tests were performed in triplicate. These experiments were designed to provide data and information on the effects of the EERC additive combined with a scavenging agent at differing doses. The test conditions are summarized in Table 1.

The samples were periodically removed from the incubator; the headspace gas of the samples was sampled with a gas-tight syringe and analyzed using gas chromatography to determine the methane, carbon dioxide, and hydrogen sulfide content of the generated biogas.

Results of the first set of laboratory screening experiments are illustrated in Figures 1 and 2. Figure 1 illustrates cumulative methane production versus time, and Figure 2 is cumulative hydrogen sulfide versus time. After 18 days of incubation, all test conditions showed an increase in the amount of methane generated and a significant decrease in the amount of sulfide in the headspace gas.

A second set of screening experiments was conducted on a different batch of Haubenschild Farm Dairy manure. The manure sample was not representative of actual manure that would be produced during normal operations but was used in screening experiments to determine the effects of a lower scavenger dose in conjunction with the additive. Test conditions for the second experiment are shown in Table 2. Experiment 2 samples were incubated for 27 days. Figures 3 and 4 are plots of the second set of laboratory screening experiments.

Table 1. Experimental Design for Laboratory Screening – Experiment 1

Condition	Fresh Manure, g	Seed, g	Additive, units of concentration	Scavenger, units of concentration
Seeded Control	36	4	0	0
Seeded Scavenger	36	4	0	2
Seeded Additive	36	4	0.5	0
Seeded Scavenger Plus Additive	36	4	0.5	2

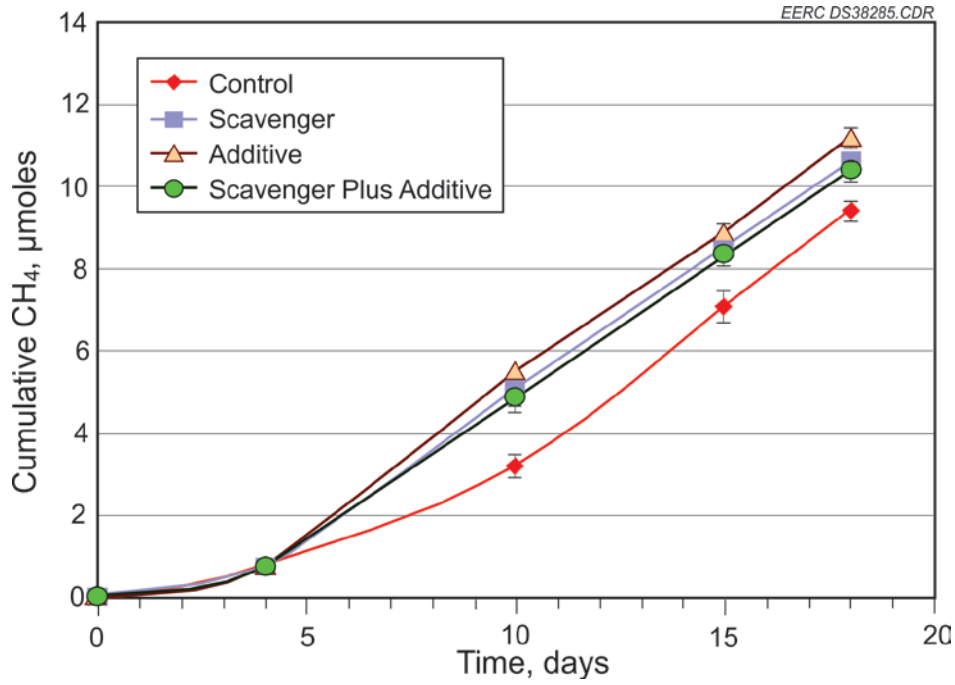

Figure 1. Effects of the scavenger and additive dosages on methane production in serum bottles fed Haubenschild Manure. The error bars represent the standard error of the triplicates. Where not shown, the error bars are within the symbols.

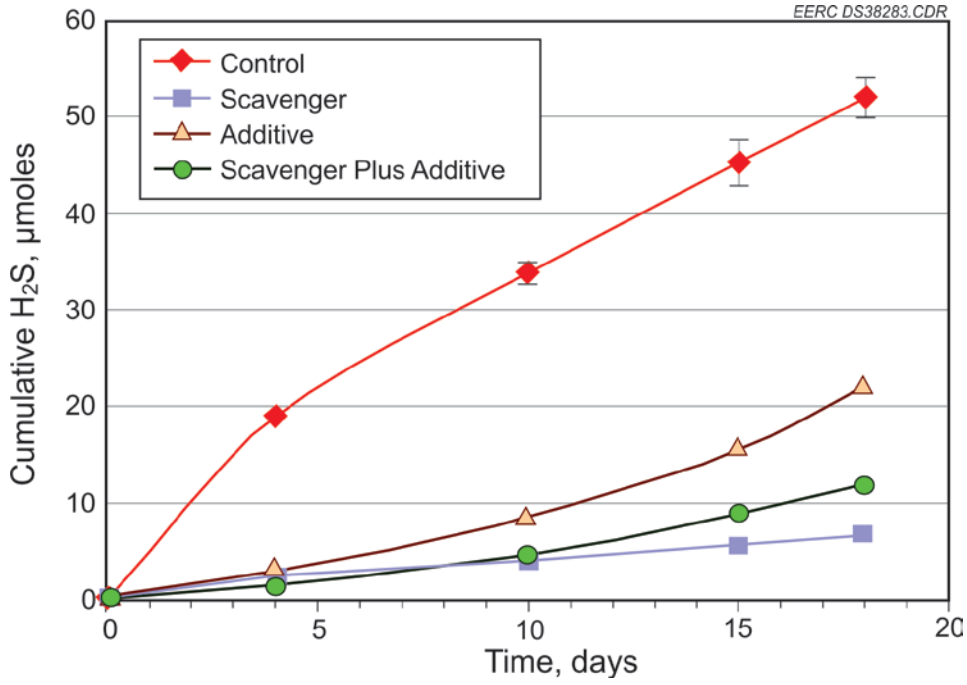

Figure 2. Effects of the scavenger and additive dosages on hydrogen sulfide production in serum bottles fed Haubenschild manure. The error bars represent the standard error of the triplicates. Where not shown, the error bars are within the symbols.

Table 2. Experimental Design for Laboratory Screening – Experiment 2

Condition	Fresh Manure, g	Seed, g	Additive, units of concentration	Scavenger, units of concentration
Seeded Control	36	4	0	0
Seeded Scavenger	36	4	0	2
Seeded Additive	36	4	0.5	0
Seeded Additive and Scavenger	36	4	0.5	1
Seeded Additive and Scavenger	36	4	0.5	2

Again, all test conditions showed a higher methane content in the headspace gas and significantly reduced sulfide. One unit of scavenger with the additive appeared to provide a benefit similar to that of 2 units. Additional screening experiments will be conducted to confirm these results on a more representative manure sample when it becomes available.

Bench-Scale Digester Experiments

Bench-scale digester experiments were continued during this reporting period using manure samples collected from the Riverview Dairy near Morris, Minnesota. The experiments were design to compare the effects of the scavenger on biogas quality. Results comparing steady-state

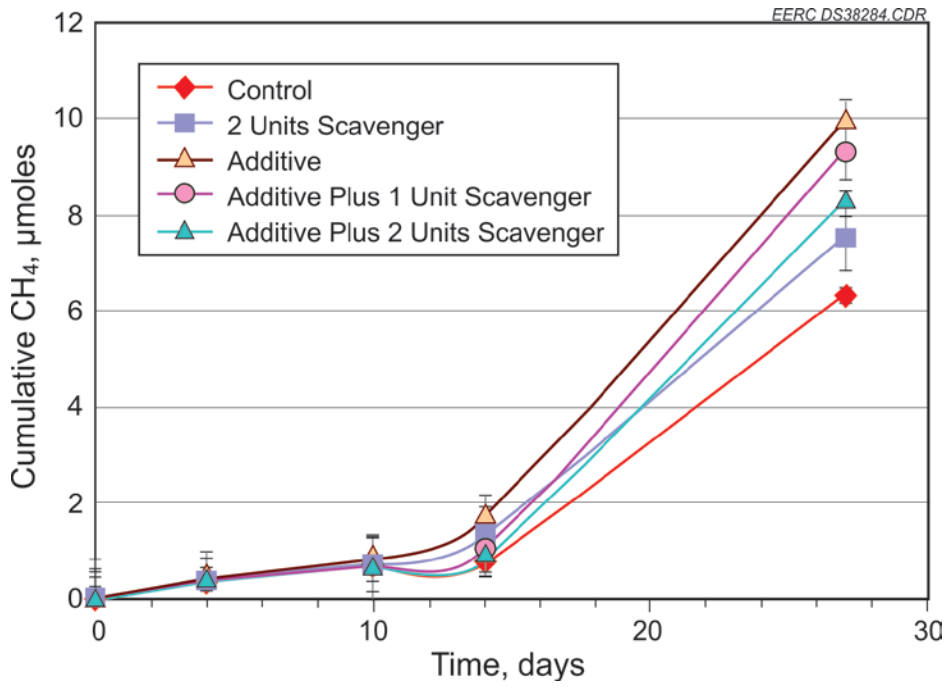

Figure 3. Effects of additive and varying scavenger dosage on methane production in serum bottles fed Haubenschild manure. The error bars represent the standard error of the triplicates. Where not shown, the error bars are within the symbols.

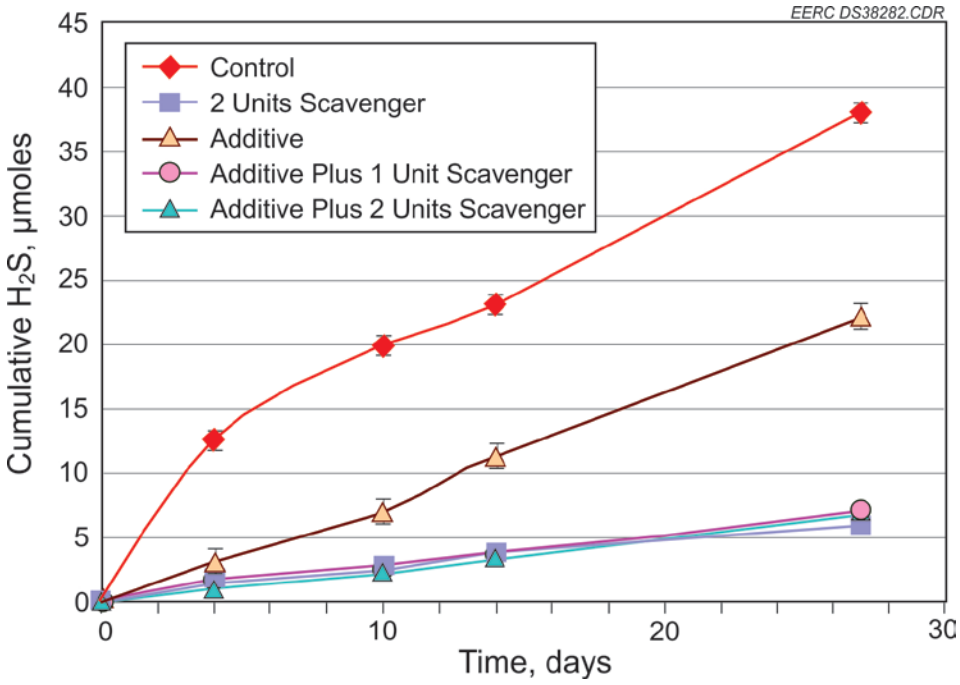

Figure 4. Effects of additive and varying scavenger dosage on hydrogen sulfide production in serum bottles fed Haubenschild manure. The error bars represent the standard error of the triplicates. Where not shown, the error bars are within the symbols.

operating data from the control and experimental digesters at a 15-day residence time incorporating a 10% digestate recycle at 2 units of scavenger are presented in Table 3.

A greater biogas flow rate in the experimental digester created a nearly 21% increase in methane production. While the H_2S concentration in the biogas was reduced by 46% in the experimental digester, overall production was reduced by 35%, again attributed to the higher biogas flow observed in the experimental digester. These results were not consistent with those of the laboratory screening experiments under similar test conditions (reported previously) using Riverview Dairy manure samples.

Table 3. Comparison of Average Steady-State Operating Data from the Bench-Scale Digesters

Parameter	Control Digester	Experimental Digester	Percent Difference
Biogas Flow, mL/min	48	58	20.8
Methane, %	57	57	–
Carbon Dioxide, %	42	43	–
Hydrogen Sulfide, ppm	6750	3640	46.1
Mass of CH_4 Produced, g/day	26.8	32.4	20.9
Mass of H_2S Produced, g/day	0.68	0.44	35.3

Pilot-Scale Digester

During this reporting period, a pilot-scale digester system was designed and fabricated at the EERC. Shown in Figure 5 during construction, the digester system is a 24-inch diameter, 20-foot-long insulated polyvinyl chloride test vessel. It has a total volume of 470 gallons (1779 liters) and a nominal operating volume (half full) of 235 gallons (889 liters).

A computer data acquisition interface was developed and is shown in Figure 6. The volume of manure in the digester will be monitored using three equidistant load cells to measure the mass of the digester. The feed and effluent rate can then be adjusted to maintain a desired retention time and correct volume to assess gas production. Biogas will be directed through a condensing heat exchanger to remove the moisture before flowing to a mass flow meter which will measure and record biogas production. The biogas will then be combined with the flow from the full-scale digester and burned in the dairy's genset engine.

The digester contents will be heated by circulating hot water through one of two heating tubes in the digester. One of the heating tubes (attached to Valve 2) runs the entire length of the digester, and a second tube (attached to Valve 1) is used to heat the incoming feed being introduced into the digester. The valves on the heating tubes control the flow of hot water through the tubes and are opened and closed depending on the temperature measurements of thermocouples TC1 and TC2. The hot water will be connected to and supplied from Haubenschild's digester system.

The pilot digester will be fed daily by diverting a portion of the manure from the dairy digester feed stream to a calibrated translucent hopper. Routine daily operations will include adding feed

Figure 5. Photograph of pilot-scale anaerobic digester vessel during construction.

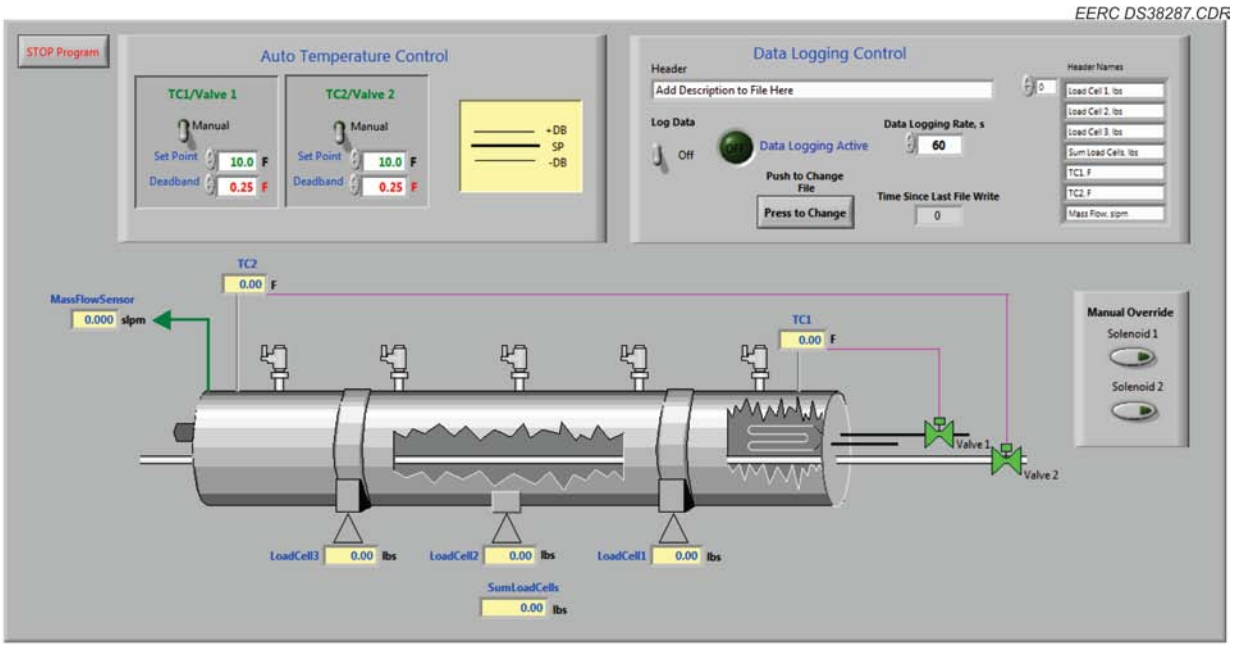

Figure 6. Pilot-scale anaerobic digester data acquisition interface

manure and removing an appropriate volume of digested manure, collecting digester biogas samples, and measuring and recording pH of feed and digested manure samples. Measurements of digester temperature, mass, and gas flow will be done continuously via the computer data logger. EERC additive and/or scavenger will be added to the manure fed to the digester. Biogas samples will be analyzed weekly during acclimation periods and daily during steady-state operation for the determination of CH_4, CO_2, and H_2S content. Total volatile solids of the feed and digested manure will be analyzed three times per week to determine volatile solids destruction. Alkalinity of the manure will also be measured periodically.

Additional Milestones: None.

Project Status: Although minor technical difficulties have been encountered, the project remains on schedule and within budget, close to the projected spending plan. Key milestones for the upcoming quarter include the installation and initiation of testing of the pilot-scale anaerobic digester at Haubenschild Farm Dairy, near Princeton, Minnesota.

LEGAL NOTICE

ASSUME NO LEGAL LIABILITY FOR THE INFORMATION IN THIS REPORT; NOR DOES ANY PARTY REPRESENT THAT THE USE OF THIS INFORMATION WILL NOT INFRINGE UPON PRIVATELY OWNED RIGHTS. THIS REPORT HAS NOT BEEN APPROVED OR DISAPPROVED BY NSP NOR HAS NSP PASSED UPON THE ACCURACY OF ADEQUACY OF THE INFORMATION IN THIS REPORT.