

January 29, 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 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/kal

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: 4 Report Date: January 29, 2010

Principal Investigator: Daniel Stepan Contract Contact: Tobe Larson

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

Congressional District: Not Applicable

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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 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., Princeton, Minnesota, to conduct the project.

During this reporting period, key milestones included the initiation of bench-scale experiments to compare process performance of control and experimental plug flow anaerobic digesters. Project funding was provided by customers of Xcel Energy through a grant from the Renewable Development Fund.

Technical Progress:

Bench-Scale Digester Experiments

Digester Operation and Maintenance

The objective of the bench-scale testing is to conduct semicontinuous biodigester experiments to verify laboratory screening test results on a larger-scale process and to optimize operational parameters in preparation for pilot-scale tests. Two identical bench-scale digester systems were constructed, shaken down, and are being used to assess performance of the EERC additive: a control digester that is being fed untreated manure and an experimental digester that is being fed manure treated with the EERC additive. Each system consists of a temperature-controlled, insulated, 8-inch-diameter by 10-foot-long polyvinylchloride bench-scale digester with

an operating volume of 13 gallons (49 L), biogas condenser for moisture removal, and continuous biogas flow metering. The biogas is vented to atmosphere through a laboratory fume hood.

A digester operation and maintenance schedule was established and is presented in Table 1. Routine daily operations included adding feed manure and removing an equal volume of digested manure, collecting digester biogas samples, measuring and recording pH of feed and digested manure samples, and measuring and recording digester temperature. In order to maintain a 20-day retention time, approximately 2.5 liters of digested manure was removed from the respective digesters every day, and an equivalent amount of fresh manure was added.

Approximately 400 mL of digested manure was blended with the feed manure of each system to ensure an acclimated population of bacteria and to provide enhanced digestion. A 1-mL volume of the EERC additive was added to the manure fed to the experimental digester.

Biogas samples are analyzed three to five times a week for the determination of methane (CH_4), carbon dioxide (CO_2), and hydrogen sulfide (H_2S) content. Fresh manure samples are collected from the dairy every other week and stored at 4°C to ensure a relative freshness of the feed manure. The manure is preheated to 38°C prior to being fed to the respective digesters.

Testing Results and Discussion

In early October, samples of both digested manure and fresh manure were collected from the Haubenschild Farm Dairy in Princeton, Minnesota. The samples were transported to EERC laboratories in 55-gallon polyethylene drums. The digested manure sample was used to seed both bench-scale digesters. A 49-L volume of digested manure was transferred under anaerobic conditions (nitrogen purge) directly into the control digester. A second 49-L volume of manure was treated with the EERC additive and transferred to the experimental digester. Both digesters were then allowed to reach a design equilibrium temperature of 38°C .

A temperature difference of nearly 2°F between the control and additive digesters was noted after the temperatures reached equilibrium. This was a concern because of the potential increase

Table 1. Operation and Maintenance Schedule for the Test Digesters

Maintenance Procedure	Frequency
Measure and Record Digester Temperature	Daily
Measure and Record pH of Feed and Digested Manure	Daily
Add Feed Manure to Each Digester System	Daily
Remove Digested Manure from Each Digester System	Daily
Collect Biogas Samples	3–5 times/week
Measure and Adjust Digester Manure Level in Digesters	Weekly
Calibrate pH Meter	Weekly
Obtain Fresh Manure (digester feed)	Twice each month

in bioactivity with increasing temperatures. Several measures were undertaken to resolve the temperature difference, including the installation of additional heat-exchange tubing and modification of the digester insulation method. With the additional heat-exchange tubing and by insulating both digesters as one unit (Figure 1), a temperature difference of $\pm 0.5^{\circ}\text{F}$ was able to be maintained.

In mid-November, after the digesters had arrived at a pseudo steady-state operating condition, fresh feed manure was acquired from Haubenschild, Farm Dairy, and gas sampling and analysis was initiated. A significant increase in H_2S in the biogas from both the control and additive digesters was noted on November 23 (Figure 2). Communication with the Haubenschild Farm Dairy revealed that it had begun the practice of using ground waste gypsum wallboard (calcium sulfate) as an animal stall bedding amendment and continued that practice from November 1 through November 19, a time coincident with a fresh manure sampling event. The bedding material ultimately gets incorporated into the digester feed manure. The result is a foreign source of sulfate (SO_4) being introduced into the manure that feeds the anaerobic digester. Sulfate is a preferred electron acceptor for sulfate-reducing bacteria (SRB) and encouraged growth of SRB. The higher sulfate levels, in turn, caused an increase in H_2S concentration of the biogas in both the Haubenschild Farm Dairy digester and the bench-scale control digester. Examination of the Haubenschild Farm feed manure indicated the presence of gypsum particles up to 3/8" diameter. The use of manure from the Haubenschild Farms to feed the bench-scale digesters was halted, and manure from a nearby dairy (Dusty Willow Dairy, Lakota, North Dakota) was utilized as an interim feed while arrangements were made with an alternative dairy in Minnesota to provide manure for the project. Increasing biogas H_2S levels continued unabated with the Dusty Willow



Figure 1. Reconfigured bench-scale digesters.

Dairy manure feed. As seen in Figure 2, the design dose of the EERC additive was initially able to provide some level of sulfide control, but the higher SO_4 levels in the feed manure eventually resulted in high H_2S levels in the biogas. The high sulfide levels eventually resulted in inhibition of biological activity, resulting in a significant decrease in biogas production. The system upset was accompanied by low CH_4 and high CO_2 content in the biogas. It was assumed that a significant amount of gypsum remained resident in the bench-scale digesters and that it would need to be removed because it would provide a long-term source of SO_4 not normally present in dairy manure.

The EERC contacted Riverview Dairy, located in Morris, Minnesota, and they agreed to provide manure for the project on an interim basis until Haubenschild Farm Dairy was able to restore proper operation to its anaerobic digester. In early December, the digesters were emptied, cleaned, and refilled with anaerobically digested manure collected from Riverview Dairy. Fresh manure was also collected from Riverview Dairy and began to be used as digester feed. The bench-scale digesters operated well on this manure for about a week when biogas H_2S levels were observed to increase in the experimental (additive) digester, while they remained relatively consistent in the control digester (Figure 3). This observation was accompanied by an increase in CO_2 and a decrease in CH_4 in the additive digester. Eventually, the CO_2 concentration exceeded the CH_4 concentration. An evaluation of the cause of this phenomenon is currently under way and will be reported in subsequent milestone reports. It may be that all the gypsum was not effectively removed from the additive digester in the cleaning process, and the digester may need to be cleaned again.

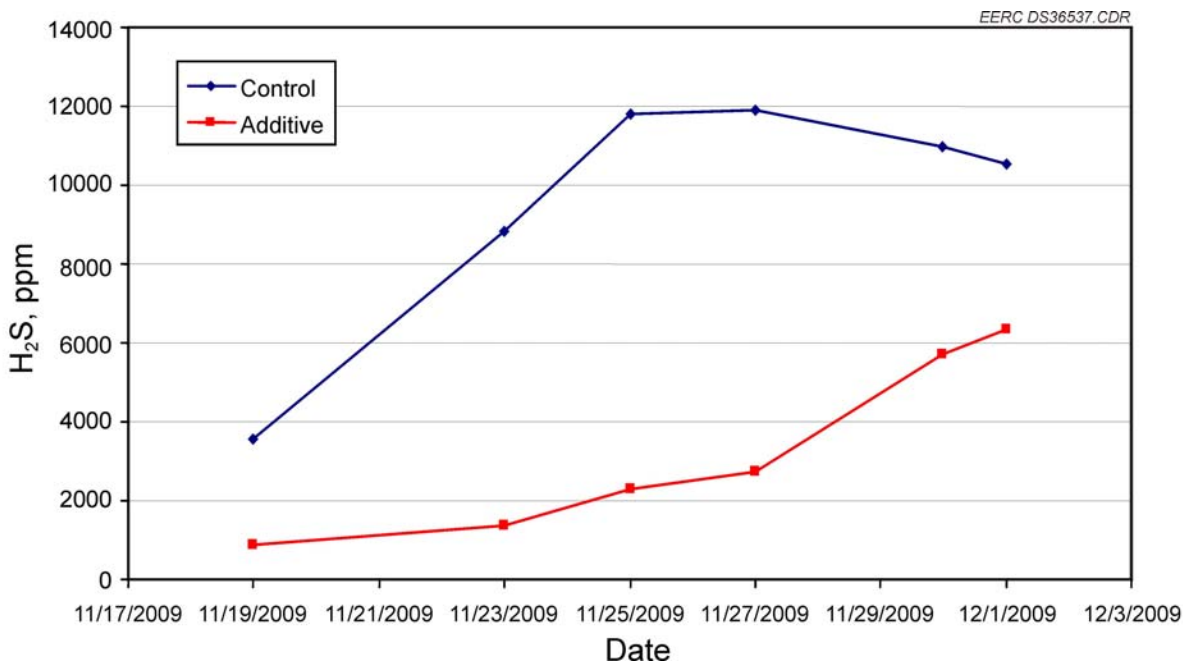


Figure 2. Bench-scale digester biogas H_2S concentration on Haubenschild Farm's Dairy manure.

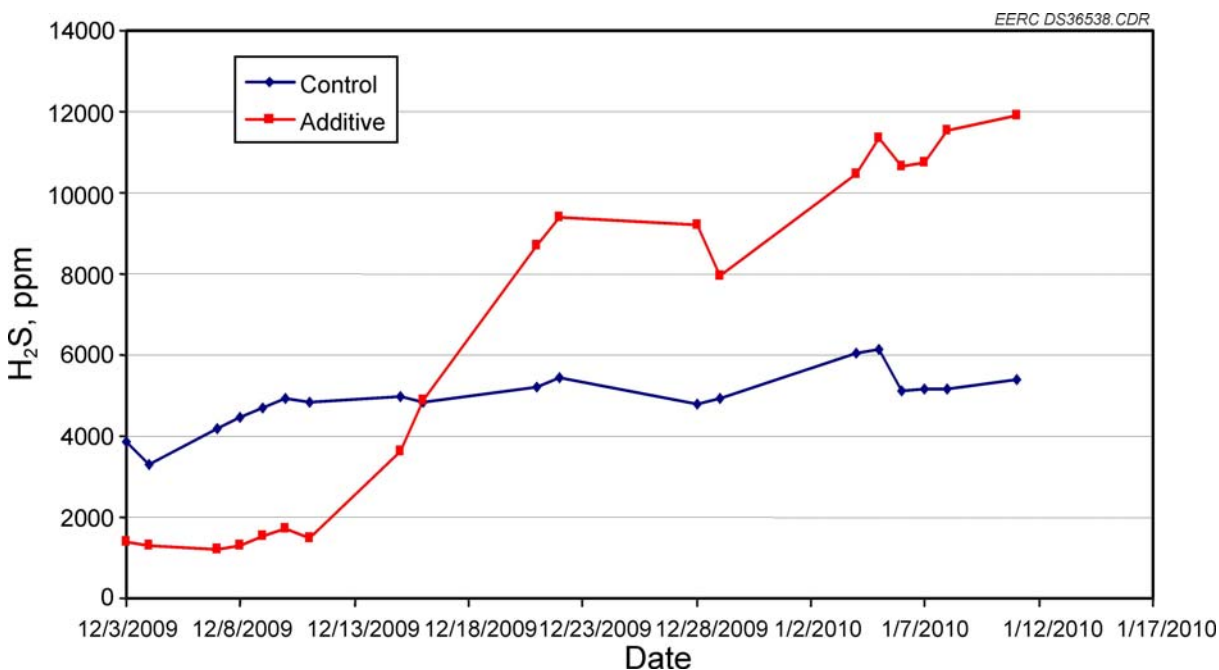


Figure 3. Bench-scale digester biogas H₂S concentration on riverview dairy manure.

Additional Milestones: None.

Project Status: Although difficulties have been encountered, the project remains on schedule and within budget. Key milestones for the upcoming quarter include the continuation of bench-scale anaerobic digestion experiments and to document experimental results to date.

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