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

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FINAL REPORT

Executive Summary:

Introduction

Anaerobic digestion of biomass is an attractive method to produce methane from biomass for combined heat and power (CHP) applications. By producing methane and combusting it in an internal combustion engine for heat and electricity generation, anaerobic digestion processes can minimize disposal costs of biomass wastes while generating clean renewable energy. Controlling pollutants, such as sulfur compounds, is key in keeping these types of biogas systems running.

This project tested and demonstrated a novel biotechnology additive to be used during the anaerobic digestion process that would increase methane content and significantly reduce hydrogen sulfide. Laboratory screening experiments were conducted to establish baseline operating conditions. Operational testing was conducted with a laboratory-scale digester at the Energy & Environmental Research Center (EERC) and expanded to a pilot-scale test and performance evaluation at the Haubenschild Farm Dairy, located near Princeton, Minnesota.

Laboratory screening experiments were devised and conducted to determine an optimal dose of a proprietary sulfide-reducing additive using dairy manure samples collected from both the Haubenschild farm operation and Riverview Dairy near Morris, Minnesota. Based on the results of laboratory screening experiments, two laboratory-scale plug-flow digester systems were designed, fabricated, and used for additive performance screening tests, which demonstrated a 46% reduction in biogas sulfide concentration and a 20% increase in methane generation rate. An even larger pilot-scale test was set up and operated for 100 days at the Haubenschild farm to demonstrate the commercial application of the additive and determine system operational sensitivity to daily differences in manure character and manure moisture content on additive performance.

Benefits

The project outcomes were many, including the promotion of small-scale renewable electricity generation, demonstration of odor control, production of a stabilized biosolid product suitable for use as bedding material or soil amendments, production of a nutrient-rich liquid product that can be used as fertilizer, and development of a method for the reduction of hydrogen sulfide gas. These findings are beneficial by:

- Developing a process to reduce sulfides by 46% in biogas while increasing methane generation by 20%.
- Reducing equipment corrosion and regional haze that result from combusting sulfides.
- Mitigating zoning requirements for anaerobic digesters by providing odor control.
- Effectively reducing the carbon footprint of a typical dairy by up to 45%.
- Transference of the technology to other industrial applications that generate high-strength processing wastewaters such as processing facilities for sugar beets, potatoes, meat and poultry, and municipalities.

Value and Opportunities

A properly operating anaerobic digester is a technologically simple system that requires relatively little operator attention, making it suitable for applications where biomass waste is produced. The biogas, however, contains varying amounts of hydrogen sulfide, a toxic gas that contributes to foul odors, causes problems with power generation equipment and when combusted, is oxidized to sulfur dioxide, a corrosive air emission that creates acid rain. Concentrations of hydrogen sulfide observed during pilot testing could correspond to as high as 80% reduction in sulfur dioxide emissions when the biogas is combusted. Minnesota has 400 dairy operations that have more than 200 cows each, which includes a total of over 223,000 cows (U.S. Department of Agriculture, 2007). The manure generated by those cows represents nearly 27 million pounds/day of renewable fuel that could provide a significant market opportunity for renewable energy production using anaerobic digestion.

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

Technical Progress:

Laboratory Screening Experiments

Objectives

The objectives of the proposed laboratory screening experiments were to:

i. Determine the effects of different EERC additive doses on the anaerobic digestion of manure (active ingredient studies).

ii. Modify the EERC additive formulation for manure digestion application (scavenger studies).

iii. Examine the effects of operational parameters (e.g. temperature, hydraulic retention time [HRT]) on application of EERC additive to the anaerobic digestion of manure (temperature studies and data interpretation with respect to HRT effects).

Materials and Methods

Laboratory screening experiments were carried out in 160-mL-internal-volume serum bottles containing 45 mL of solution/slurry and 115 mL of headspace for collection of produced gas. The 45 mL of solution/slurry included 40 mL of homogenized manure and 5 mL of aqueous solution added to deliver additive and/or scavenger (or sterile distilled water in the case of the control tests). The homogenized manure was either fresh manure alone or a mixture of fresh manure and active digested manure added as a seed culture (i.e., inoculum). The digested manure came from an anaerobic seed reactor operated during the early phase of this study, the plug-flow laboratory-scale control reactor, or was effluent collected from the full-scale dairy farm digester. The mixed sample of fresh manure and seed culture was homogenized in a blender to prepare a material that could be transferred into serum bottles.

The experiments were set up in an anaerobic glove box, as shown in Figure 1. An anaerobic glove box is a flexible chamber equipped with a vacuum air lock and a system for the continuous removal of any oxygen from the chamber atmosphere. The oxygen removal system works by passing the nitrogen/hydrogen (approximately 2% H_2) glove box atmosphere across a heated palladium catalyst. This converts any oxygen that may have entered the chamber into water vapor, thus maintaining an oxygen-free environment.

All test conditions were run in triplicate. The serum bottles were sealed with butyl rubber stoppers and aluminum crimpers, removed from the anaerobic glove box, mixed using a laboratory vortex mixer, and incubated under static conditions at either 35° or 55°C in the dark. All glassware, stoppers, and other supplies were autoclaved before use to prevent contamination.

The serum bottles were periodically removed from the incubator and analyzed for gas production and gas composition. Gas volume measurements were performed using volume displacement in a wetted glass syringe. The headspace gas composition was analyzed by sampling each serum bottle using a gas-tight syringe and analyzing the sample by gas chromatography to determine the methane, carbon dioxide, and hydrogen sulfide content of the generated biogas (the gas analysis method is documented in Milestone Report 1 dated April 7, 2009).

Figure 1. EERC researchers prepare biological experiments in an anaerobic glove box.

Results from the experiments are presented as either the moles of methane and H_2S produced per gram of solids in the manure delivered to the serum bottle or as the total moles of methane and H_2S produced in a serum bottle (not divided by the solids concentration). The amount of methane produced is typically in the range of 0 to 12 millimoles (mmol) total, or 0 to 3 mmol/gram dry solids (solids concentrations in the manure are typically in the range of 7% to 9% so the serum bottles typically contain 2.8 to 3.6 grams of dry solids).

Experimental Results

The experimental results from the screening experiments are separated into three sections:

- Initial screening with manure from Haubenschild, Princeton, Minnesota
  - The experiments conducted to investigate the effect of additive concentration over a wide range resulted in the selection of 0.5 units of additive as the appropriate concentration for use with Haubenschild manure.
  - Experiments with a low concentration of scavenger for precipitation of residual H_2S provided some evidence of control during the early stage of the batch experiments but suggested too little scavenger was added to maintain scavenging capacity for the length of the experiment.
- Screening in support of bench-scale reactor experiments using manure from Riverview, Morris, Minnesota.

- The inoculum/seed culture addition experiment revealed that addition of seed culture was required to obtain effective digestion in serum bottle experiments conducted with Riverview manure.

- Scavenger addition experiments revealed that addition of scavenger along with additive resulted in further decreases in the amount of H_2S produced.

- The nutrient addition experiment which did not reveal any benefit could be derived from adding nutrients.

- Experiments conducted with the 0.5 units of additive concentration revealed that while decreased H_2S formation was observed, the amount of H_2S produced using Riverview manure was much greater than that produced using Haubenschild manure both with and without the use of the additive.

- Screening in support of the pilot-scale reactor experiments conducted at Haubenschild, Princeton, Minnesota

  - Experiments were conducted to further optimize the amount of additive and scavenger needed to control the production of H_2S during the digestion of Haubenschild manure. The results revealed additive use could be reduced to 0.25 units, with scavenger supplied at 1 unit. These results were used to select the test conditions applied for the pilot-scale testing.

Initial screening with manure from Haubenschild, Princeton, Minnesota

Effects of the "Active Ingredient" Additive on Production of Hydrogen Sulfide

The experiments were first conducted with 8, 2, and 1 units of additive concentration. A second experiment was then set up with 4, 0.8, and 0.5 units of additive concentration. In both experiments, the "no additive" group served as the control sample.

Results indicate that addition of the EERC additive over the tested concentration range significantly reduced hydrogen sulfide production (Figure 2). Figure 2 shows the cumulative production of hydrogen sulfide in the gas phase, expressed as μmol per gram of dry manure fed. As shown in Figure 2, production of hydrogen sulfide in all experimental groups was significantly reduced as compared with the control group and a higher concentration of additive led to greater reductions in H_2S production. The H_2S reduction effect was consistent at all additive doses after 5 days of incubation, with the overall effect diminishing somewhat with time. Even with the diminished effect, the overall reduction in H_2S was greater than 65% after 21 days of incubation at the lowest dose tested of 0.5 units. The EERC additive is able to effectively reduce hydrogen sulfide production at all tested experimental concentrations. These results demonstrate good hydrogen sulfide control, considering that commercial digesters typically operate at a HRT of less than 20 days.

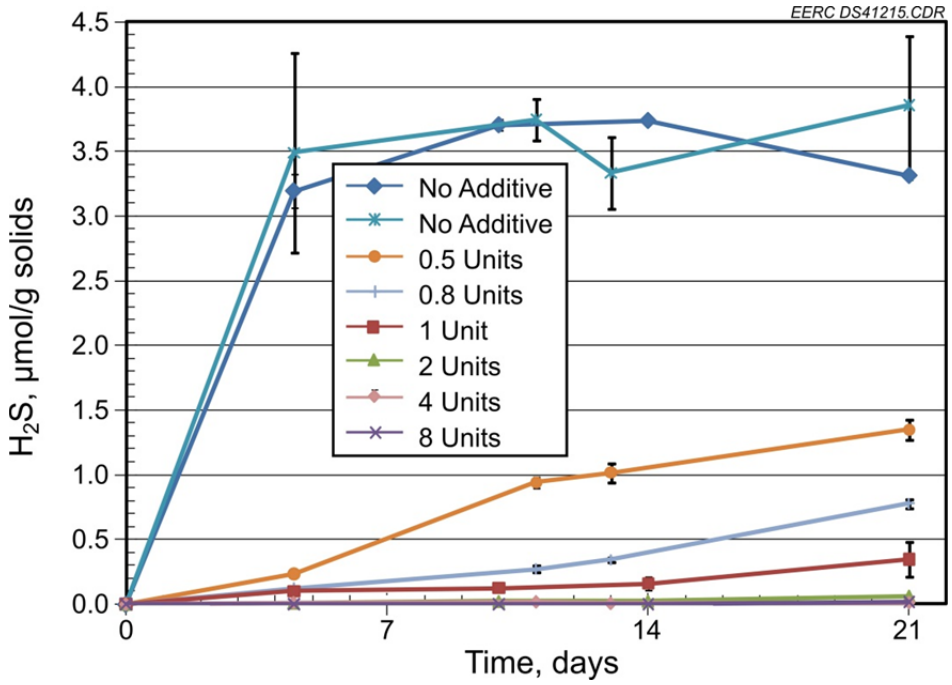


Figure 2. Effect of additive concentration on H_2S production. H_2S is presented as µmol produced per gram (dry weight) of the manure. Error bars represent standard error of of the analysis results from triplicate experiments.

Effects of the Additive on Methane Production

Figure 3 shows methane generation for the same samples previously discussed. At additive doses of 4 units or less, there did not appear to be a significant effect, either stimulatory or inhibitory, for the generation of methane. However, at an additive dose of 8 units, a possible inhibitory effect can be noted with incubation times greater than 14 days, with reduced generation of both methane and carbon dioxide. A dose this high, however, while it defines an upper limit of additive use, would most likely not be practical in commercial applications because of the high cost of chemical addition it would likely represent. It appears from these data that the hydrogen sulfide prevention additive did not have any efficacy in promoting the concomitant generation of methane. Some of the other serum bottle studies and results from the bench-scale reactor provided evidence of increased methane generation under some conditions.

Modification of the EERC Additive Formulation for Manure Digestion Application by Addition of a H_2S Scavenger

An experiment designed to test the effect of adding scavenger along with 0.5 units of EERC additive was conducted using Haubenschild manure. Scavenger was added at concentrations of 0, 0.04, 0.08, and 0.2 units.

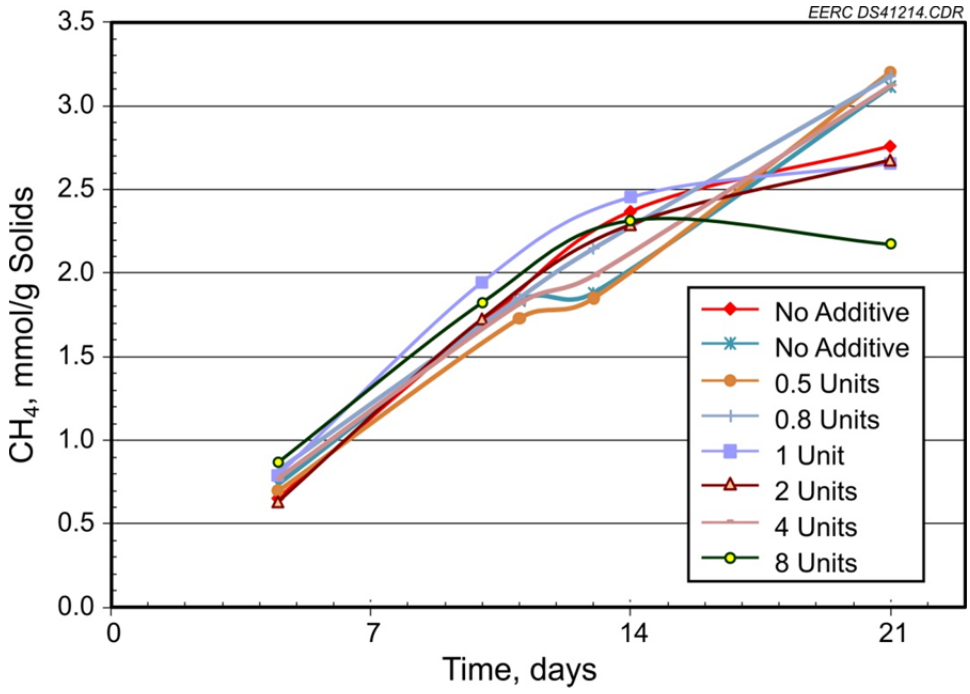


Figure 3. Effect of additive concentration on methane production. Methane production is presented as mmol of methane produced per gram (dry weight) of manure.

Figure 4 shows the manure, dry mass normalized, cumulative H_2S production observed over the course of the experiment. The results after 5 days of incubation (see Figure 5) suggested a strong negative correlation between scavenger concentrations added and the amount of H_2S produced. However, the data shown in Figure 4 appear to indicate no effect of scavenger addition over this range of scavenger concentrations.

Figure 6 illustrated that the use of low concentrations of scavenger had no discernable effect on the production of CH_4.

Based on the promising results of sulfide control during laboratory screening experiments, plans for bench-scale testing were initiated.

Screening in Support of Bench-Scale Reactor Experiments Using Manure from Riverview, Morris, Minnesota

Effects of Inoculum Size on Production of Methane and Hydrogen Sulfide

Results from previous batch serum bottle experiments and previous bench-scale digester runs suggested that decreasing the hydraulic residence time of the digesters and incorporating sludge recycle might help improve performance. Sufficient volatile solids (VS) destruction and methane

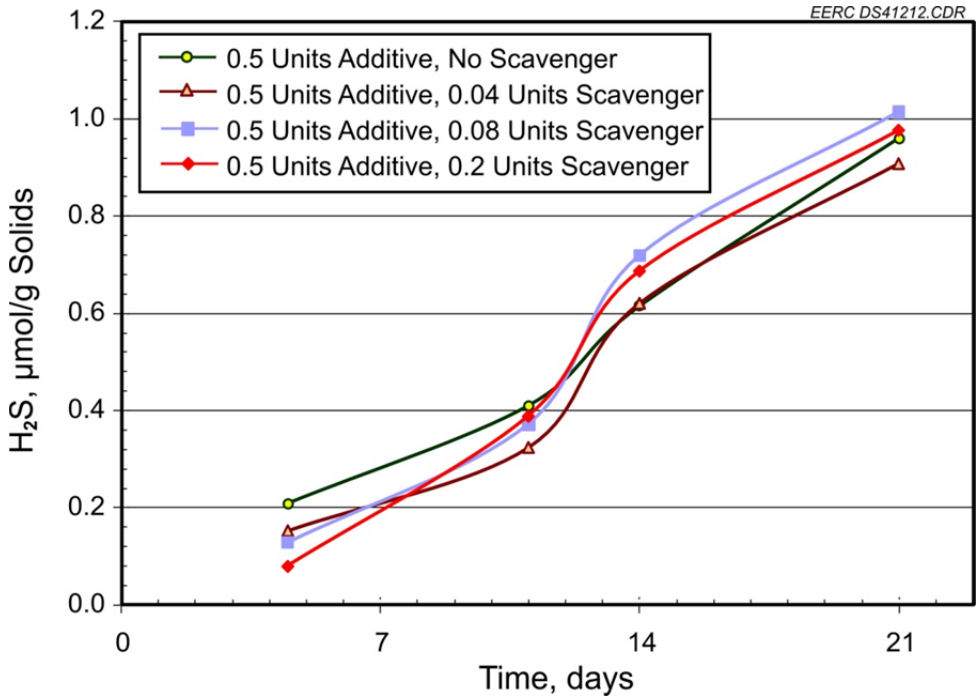


Figure 4. Effect of low concentration of scavenger addition on H_2S production. H_2S is presented as µmol produced per gram (dry weight) of manure.

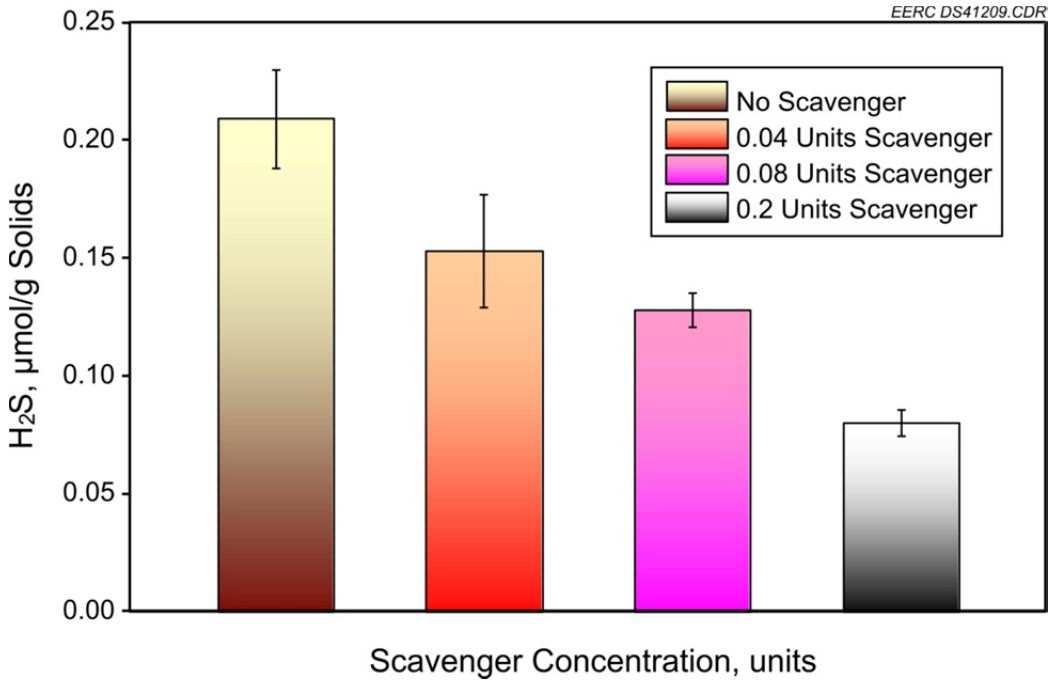


Figure 5. 5-day cumulative gas-phase hydrogen sulfide produced as a function of scavenger concentration applied along with 0.5 units of additive. H_2S is presented as µmol produced per gram (dry weight) of manure. Values are averages of triplicate samples. The error bars represent the standard deviation of the triplicates.

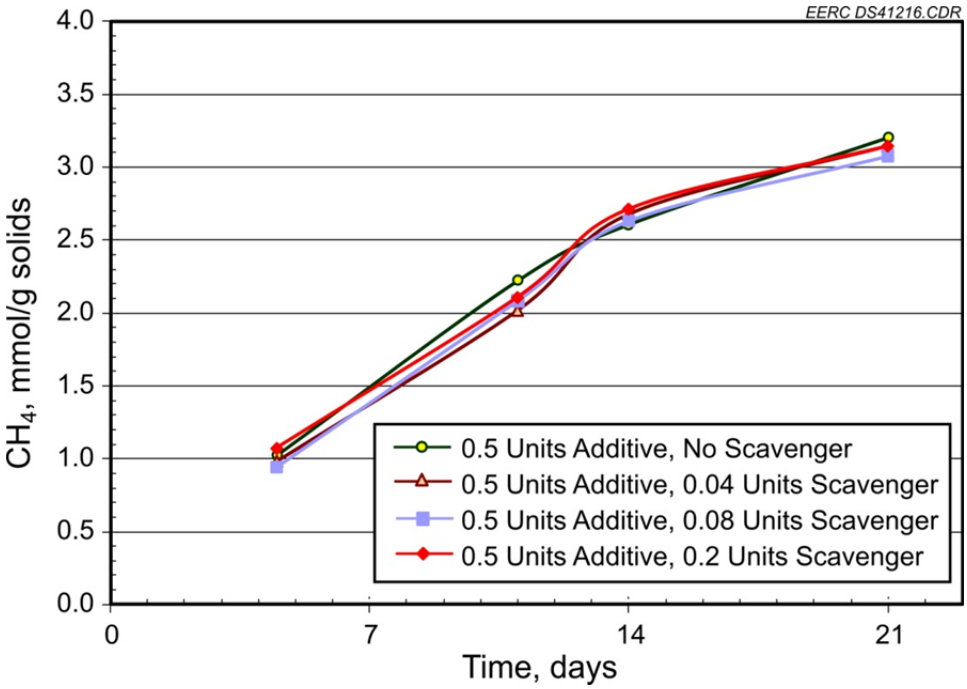


Figure 6. Effect of low concentration of scavenger addition on methane production. Methane is presented as mmol produced per gram (dry weight) of manure.

formation could be accomplished at the shorter residence time by inoculation of the fresh manure with a healthy culture of methanogenic microorganisms through the use of recycle. Further, the shorter residence time should avoid the potential for regrowth of sulfidigenic organisms that might have caused the failure of the digester in November 2009 and early in this reporting period (data not shown). Before incorporating these changes in the lab-scale plug-flow digesters, a batch serum bottle study was performed to select the appropriate recycle rate (seed culture size) and residence time. Table 1 shows the experimental design for the study. It included the use of a "no seed" control, three levels of seed addition to represent three different recycle rates, and the observation of the methane and hydrogen sulfide production in these cultures over time to represent residence time in an ideal plug-flow digester. All serum bottles received additive at the normal concentration of 0.5 units. It should be noted that real digesters have dispersion (mixing) that will minimize the need for recycle. A tracer study can be conducted on a real system to get a measure of the amount of dispersion.

Table 1. Experimental Design for Seed Size Serum Bottle Experiment

Condition	Fresh Manure, g	Seed, g	Additive, mL (0.5 units)
No Recycle, 0%	40	0	5
5% Recycle	38	2	5
10% Recycle	36	4	5
15% Recycle	34	6	5

Results of the seed size experiments are plotted in Figures 7 and 8. From Figure 7, it is apparent that recycle of digester effluent would significantly increase the rate of methane production, which could be obtained in a plug-flow digester fed the fresh manure used in this experiment. The amount of benefit obtained by increasing the % seed used was most pronounced at 10 days, where the 10% and 15% seed cultures had produced almost twice as much methane as the 5% seed culture. By 20 days, the methane production by the 5% seeded culture was similar to that observed for the 10% and 15% cultures. The unseeded (0%) cultures had produced less than 1/5 the amount of methane by Day 20 than that observed for the seeded cultures. By Day 20, the 5%, 10%, and 15% seeded cultures produced 654%, 715%, and 663% more methane, respectively, than the unseeded cultures. This very large increase in methane production is not expected to be observed for a real plug-flow reactor. Dispersion in a reactor will accomplish some amount of inoculation of the freshly added manure. Therefore, recycle in a real plug-flow digester should only provide moderate benefits.

From Figure 8, it is apparent that addition of the seed culture did not increase the production of H_2S like it increased the production of methane, thus improving the ratio of methane to H_2S in the produced gas. It is also apparent that for all three of the seeded cultures, the rate of H_2S production was very low for the first 10 days. The rate of H_2S formation appeared to increase dramatically after 10 days of incubation. These data were interpreted as an indication that the benefit of the additive may have been exhausted by 10 days, allowing for regrowth of sulfidogenic microbes.

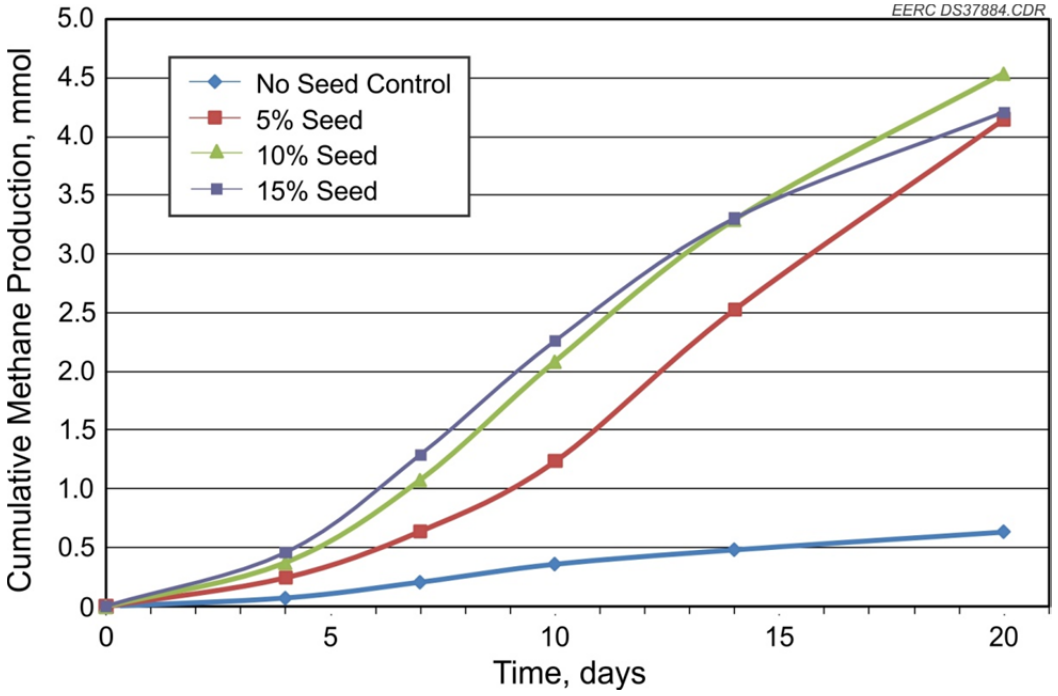


Figure 7. Effects of the inoculate (seed) size on methane production in serum bottles fed Riverview manure.

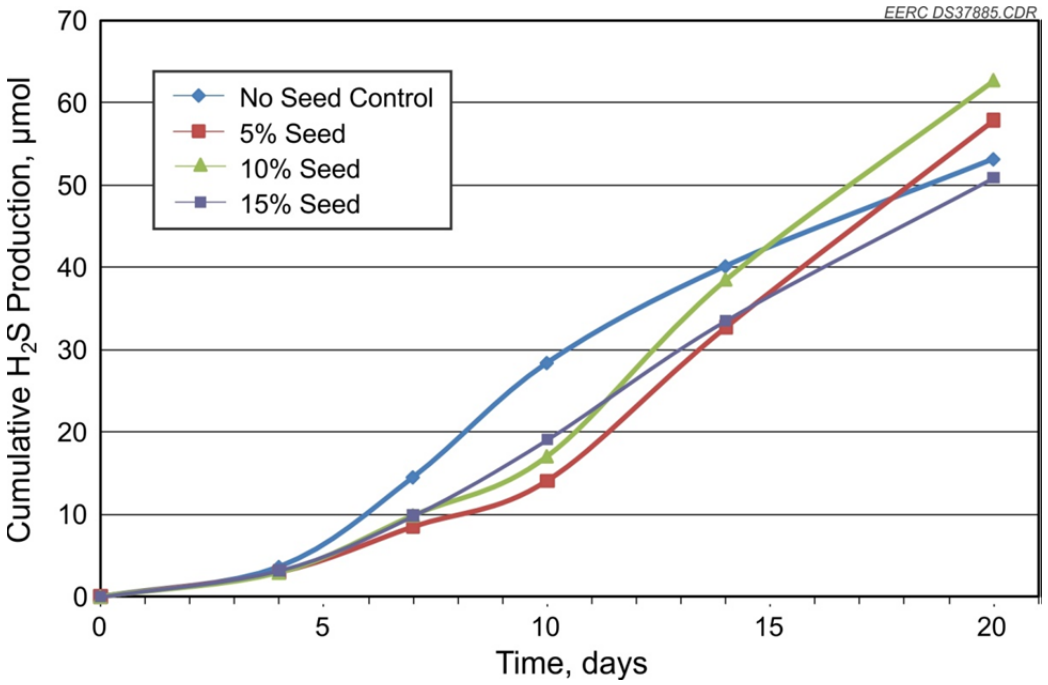


Figure 8. Effects of the inoculate (seed) size on formation of hydrogen sulfide in serum bottles fed Riverview manure.

Effects of H_2S Scavenger Addition on Production of Methane and Hydrogen Sulfide

Additional serum bottle experiments were conducted to further investigate the use of a sulfide scavenger to be added in conjunction with the EERC additive. The scavenger is designed to capture any sulfide that is produced and keep it from being emitted as H_2S. The design of this experiment is given in Table 2. The experiment included the use of seed culture at 10% additive at 0.5 units and scavenger at 0, 1, 2, and 4 units of concentration. The experiments were run for 20 days to determine if the scavenger might prevent the increased H_2S production rate observed after 10 days in the previous experiment. If it did, it might allow the use of longer residence times in the digester without the apparent sulfidogenic microorganism regrowth. The longer residence time would allow for greater VS destruction and more methane production.

Table 2. Experimental Design for Use of Scavenger in Control of H_2S Production

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

Results of the scavenger experiments are plotted in Figures 9 and 10. From Figure 9, it is apparent that addition of the scavenger had a very substantial effect on methane production. While the addition of the additive increased the 20-day methane production from 1.37 mmol for the control to 3.95 mmol, the addition of scavenger further increased this to 9.05, 11.1, and 10.7 mmol for the 1, 2, and 4 units of scavenger added, respectively. This increase in methane production as a result of scavenger addition was not expected. It is surmised that it may be because of changes in nutrient availability. Since sulfide may precipitate some nutrients as metal sulfide or sulfide complex, the addition of the scavenger should leave more nutrients available for the microorganisms. A serum bottle study designed to investigate this was performed, as described later.

Figure 10 contains the H_2S production data for the scavenger experiment. From the data presented in Figure 5, it is apparent that the additive delayed the production of H_2S, with the rate of production increasing with time of incubation as was seen in the previous serum bottle study. The 9-day cumulative H_2S generation in the additive test was 32% of that seen in the control. At 20 days, the benefit decreased to where the additive test had produced 65% of the H_2S produced in the control. For the condition where the scavenger was added at 1 unit (along with the additive), there was an additional benefit observed at 5 and 9 days of incubation but no additional benefit after 14 and 20 days. The 2 and 4 units of concentration of scavenger conditions provided almost complete control of H_2S formation for 14 days, with production of only 2.0% to 3.4% of the H_2S of the no additive control, respectively. At 20 days, the observed H_2S formation was 14% of that observed for the no additive control. These results suggest that the combined use of additive and scavenger should allow for operation of the digester at residence times of at least 14 days with almost no H_2S production and may allow for successful operation at residence times as long at 20 days with very little H_2S production.

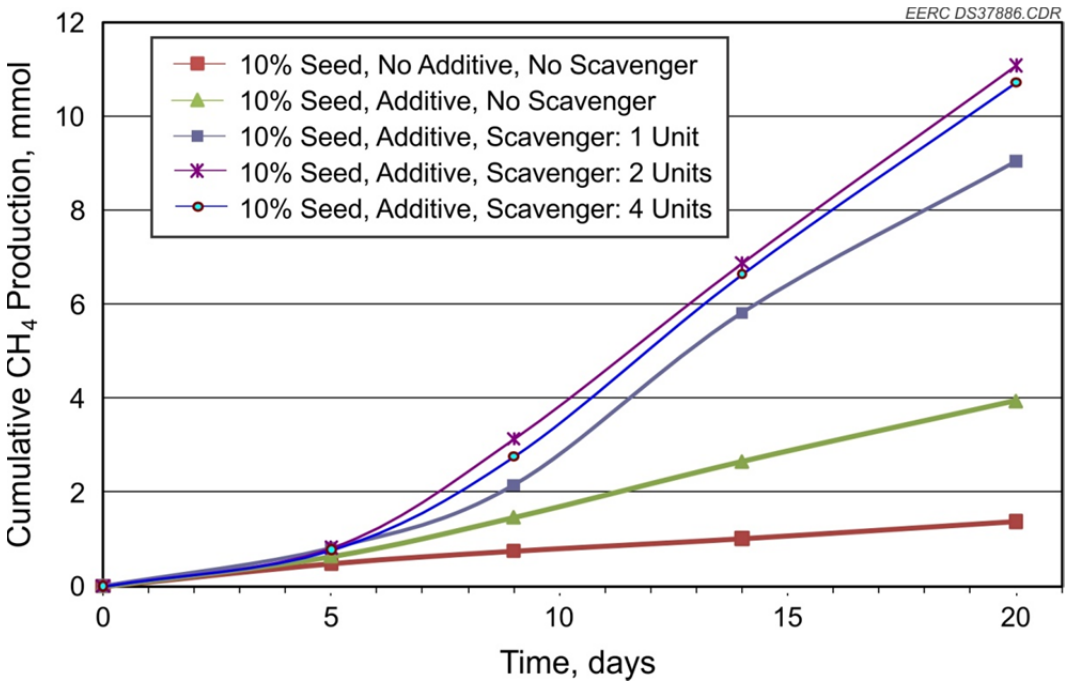


Figure 9. Effect of additive and scavenger addition on cumulative methane production in serum bottles fed Riverview manure.

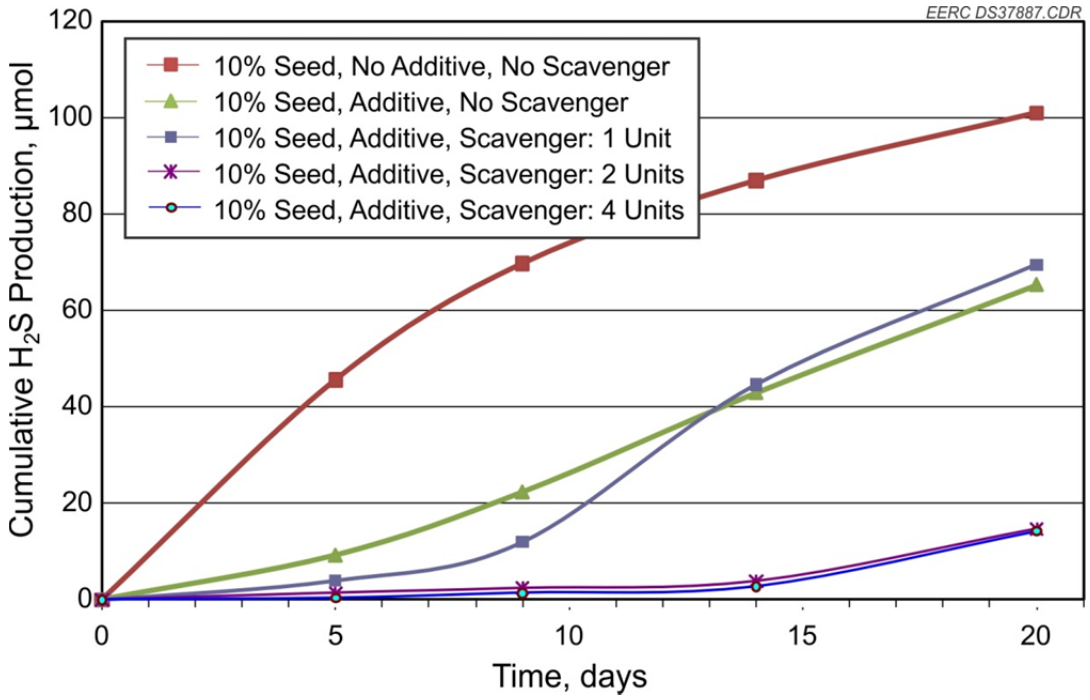


Figure 10. Effect of additive and scavenger addition on cumulative H_2S production in serum bottles fed Riverview manure.

Effect of Nutrient Addition

The results of the previous experiment suggested that addition of moderate concentrations of scavenger helped lead to increased methane generation as well as the reduction in H_2S production. Two possible reasons the scavenger might help increase methane generation were surmised:

1) Reducing sulfide toxicity on methanogens – It is well documented that sulfide is toxic to methanogens. The scavenger mitigates sulfide and thereby reduced the toxicity on methanogens.

2) Improving nutrient bioavailability – Some trace metals such as Ni (nickel) and Co (cobalt) are essential nutrients to the anaerobic microorganisms because they are components of the enzymes. Sulfide is very reactive and may react with these and other trace metals to form insoluble metal sulfide or metal sulfide complexes, which are not bioavailable to the methanogens. Addition of scavenger could sequester the sulfide, making it less available to react with nutrient metals, thus eliminating nutrient limitations.

It is not possible to independently test the first possible reason, but the potential that relief of a nutrient limitation was the cause could be tested by looking at the effect of nutrient addition on methane generation. Therefore, a nutrient addition experiment was performed to determine whether the apparent enhancement effect on methane production by the scavenger addition that

was observed in the previous experiment (Figure 9) might be due to improved nutrient bioavailability. The design of the nutrient experiment is given in Table 3. A stock solution containing a mixture of several trace metals (Mn, B, Zn, Cu, Mo, Ca, Ni, and Se) was used as the nutrient solution. The final concentrations of the metals in the manure slurry ranged from 0.05 to 0.5 mg/L.

Results of the nutrient experiment are plotted in Figures 11 and 12. As shown in Figures 11 and 12, addition of the trace metals had no effect on either methane or hydrogen sulfide production. The presence of the additive did not increase methane production but did decrease H_2S production. The addition of the nutrients did not change the results for either the no additive or with additive condition. It should be noted that the amount of methane produced in all of these experiments was similar to the amount of methane produced for the control conditions in the previous experiment. The amount of H_2S produced was greater, but the pattern observed between the control and the additive conditions was similar for both sets of experiments, indicating that enhancement of methane production by the scavenger was unlikely due to improving nutrient bioavailability.

Effect of Manure Source on Efficacy of EERC Additive

Results from the initial screening experiments were performed using manure from Haubenschild, and those done in support of the bench-scale reactor were done using manure from the Riverview, Morris, Minnesota. From running similar experiments with these two different manure sources, it appeared that there were differences in the efficacy of the additive. In order to check this, a comparison was performed using results of previous studies to see if, in fact, there was a real difference. The data selected for use in the comparison came from control (no additive) and 0.5-unit-additive-concentration serum bottle tests operated at 35°C. The comparison was made using 19.5 ± 1.5 days of incubation cumulative methane and H_2S production data. The results of the comparison are shown in Figures 13 and 14 for H_2S and methane production, respectively (average of two batches performed under the same experimental conditions).

Without the additive amendment, after 20 days of incubation, the Riverview manure produced 123.6 μmol H_2S and 1.7 mmol CH_4, compared to 41.7 μmol H_2S and 8.9 mmol CH_4 produced from the Haubenschild manure. The Riverview manure produced 196% more H_2S and 81% less CH_4.

Table 3. Experimental Design for the Nutrient Experiment

Condition	Fresh Manure, g	Seed, g	Nutrients, unit of concentration	Additive, unit of concentration	Scavenger, unit of concentration
Control	36	4	0	0	0
Nutrient	36	4	1	0	0
Additive	36	4	0	0.5	0
Additive and Nutrient	36	4	1	0.5	0

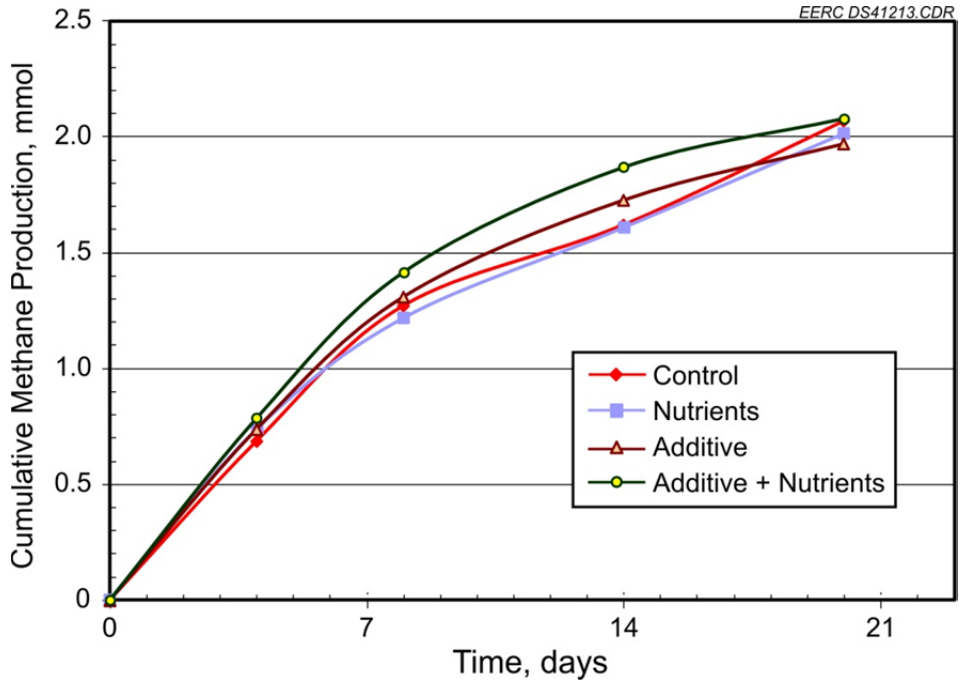


Figure 11. Effect of additive and nutrient addition on cumulative methane production in serum bottles fed Riverview manure.

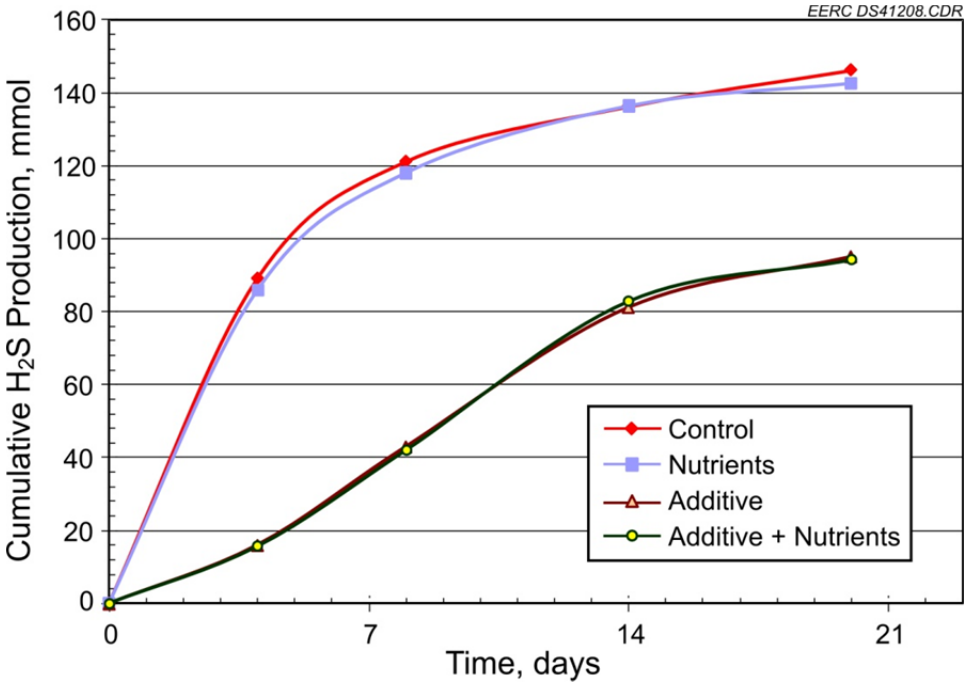


Figure 12. Effect of additive and nutrient addition on cumulative H_2S production in serum bottles fed Riverview manure.

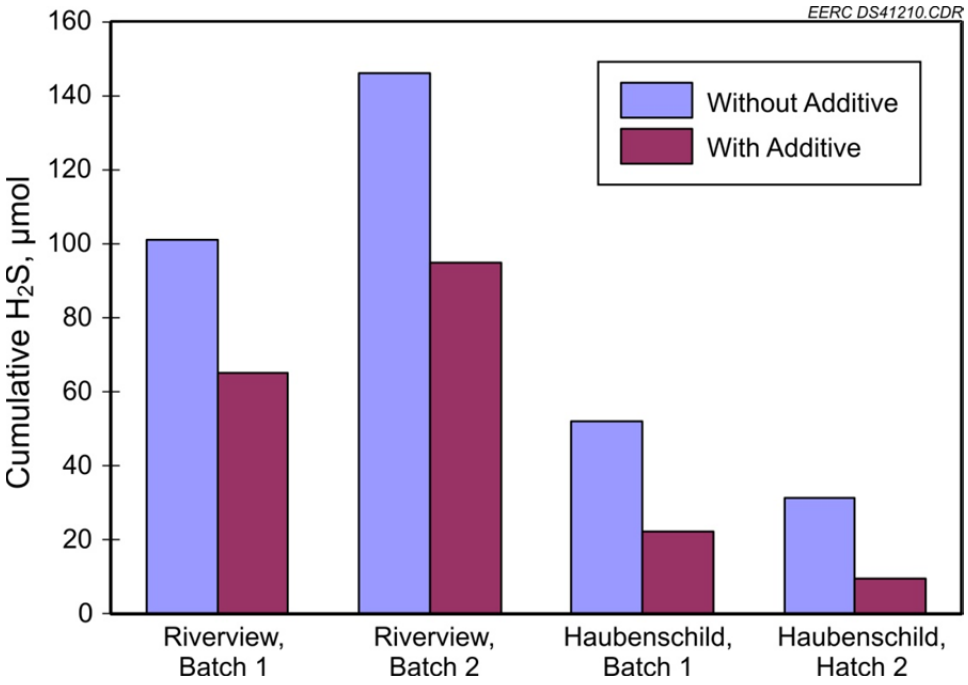


Figure 13. Comparison of the effect of manure source on the formation of H_2S with and without use of 0.5 units of additive.

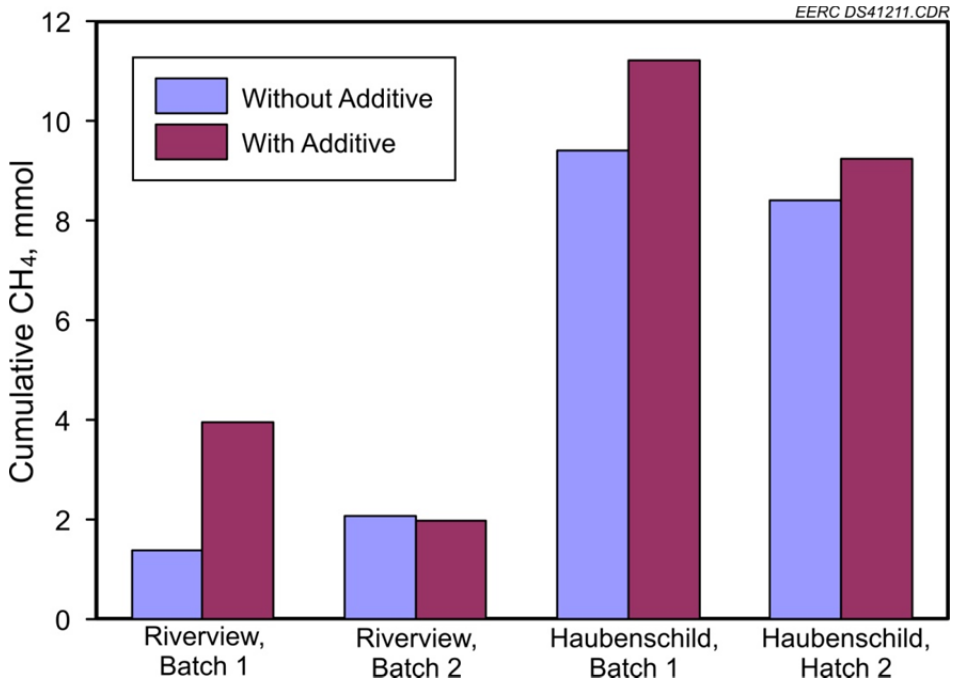


Figure 14. Comparison of the effect of manure source on the production of methane with and without use of 0.5 units of additive.

During the anaerobic digestion processes, production of H_2S and CH_4 is determined by many factors, including the concentration of sulfate, amount of organic sulfur in the substrates, microbial community structure and population sizes of sulfate-reducing bacteria (SRB) and methanogenic bacteria, nutritional conditions, presence of inhibitors/stimulators of SRB or methanogens, etc. Among these factors, sulfate and total sulfur level in the substrate are usually the major factors affecting H_2S and CH_4 production. It was unclear what factors in the Riverview and Haubenschild manures caused the significant differences in H_2S and CH_4 production; however, since sulfate and sulfur levels are usually the major factors affecting H_2S and CH_4 production, it is likely that the Riverview manure contained more sulfate and/or total sulfur.

Since Riverview and Haubenschild manures had different H_2S production capabilities, the effects of the additive on these two manures were different. With the amendment of the same additive dose, after 20 days of incubation, 63.4% (average of two batches) H_2S reduction in the Haubenschild manure was observed; however, only 35.2% reduction in the Riverview manure was apparent.

While significant differences in H_2S and CH_4 production on manure from different dairies was evident, variation in H_2S and CH_4 production among different sample batches of manure from the same dairy was also observed. For example, after 20 days of incubation, Batch 1 Riverview manure produced 101.0 μmol H_2S and 1.4 mmol CH_4, while Batch 2 produced 146.2 μmol H_2S and 2.1 mmol CH_4. The H_2S produced from Batch 2 Riverview manure was 44.7% more than that produced from Batch 1. Similar results were also observed with the Haubenschild manure, without the additive amendment, Batch 2 Haubenschild manure produced 65.0% more H_2S than Batch 1 manure did. However, compared to the variation in H_2S and CH_4 production caused by manure sources, the variation caused by sample batches was much smaller.

Despite the variation caused by different sample batches, it appeared that the effects of the additive on the same source of manure were relatively stable. Calculation on the standard error (SE) showed that the SEs in H_2S reduction for the Riverview and Haubenschild manures were 0.5% and 9.8% of their respective means; in contrast, the SE between the two manures was 28.6% of the mean.

Results of the screening experiments conducted with two sources of manure showed that the effects of the additive on H_2S mitigation and CH_4 enhancement were manure-dependent. Even though differences in sample batch may cause some variation in H_2S and CH_4 production, the effects of the additive on the same source of manure were relatively stable.

Screening Studies Performed in Support of the Pilot-Scale Tests

Because pilot-scale tests were to be performed at Haubenschild in Princeton, Minnesota, and results of previous screening studies appeared to indicate the appropriate additive and scavenger formulation might be influenced by the characteristics of the manure, additional screening experiments were conducted using Haubenschild manure collected during final preparations for the pilot-scale test.

Three sets of experiments were conducted. The results of those experiments are given here.

Results of the first set of the final three laboratory screening experiments (Table 4) are illustrated in Figures 15 and 16. Figure 15 illustrates cumulative methane production versus time, and Figure 16 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 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 5. Experiment 2 samples were incubated for 27 days. Figures 17 and 18 are plots of the second set of laboratory screening experiments.

Table 4. Experimental Design for Laboratory Screening – Pilot 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 and Additive	36	4	0.5	2

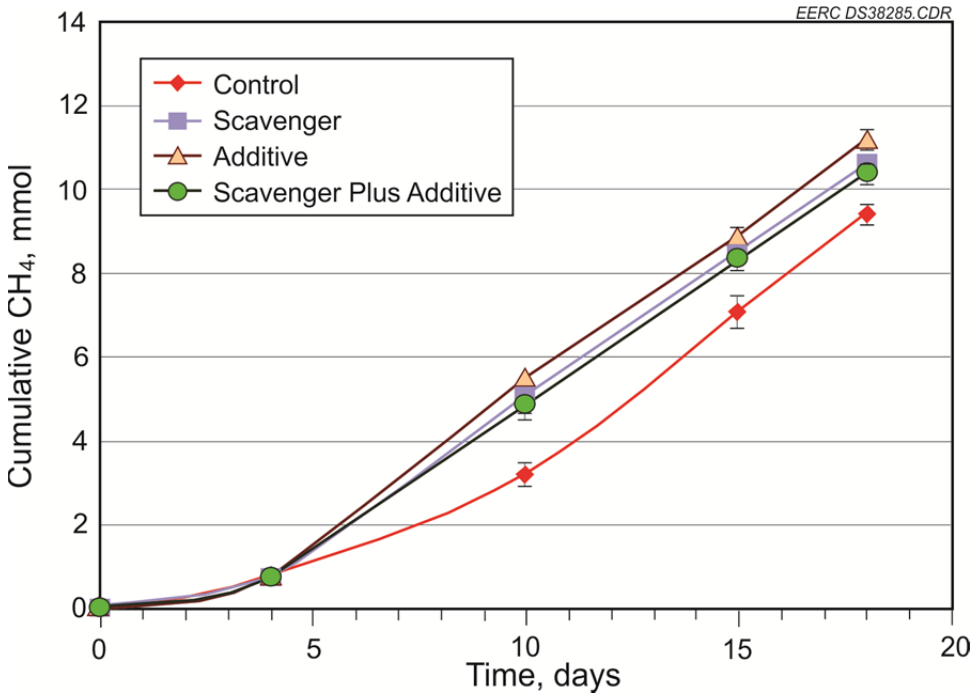


Figure 15. Effects of the scavenger and additive dosages on methane production in serum bottles fed Haubenschild manure. The error bars represent the standard error of the triplicates. Where not shown, the error bars are within the symbols.

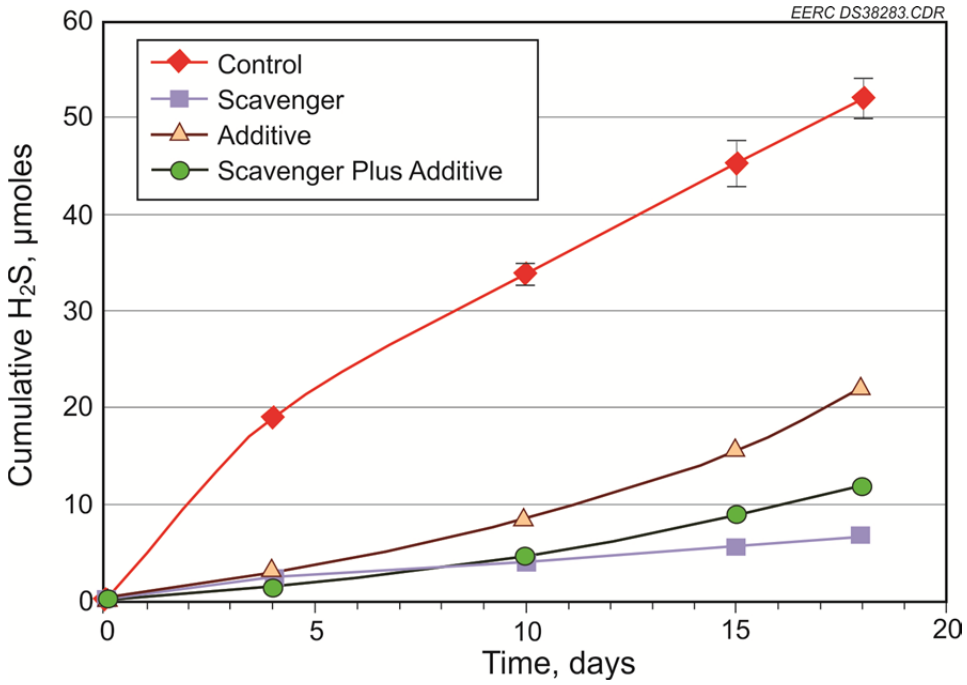


Figure 16. Effects of the scavenger and additive dosages on hydrogen sulfide production in serum bottles fed Haubenschild manure. The error bars represent the standard error of the triplicates. Where not shown, the error bars are within the symbols.

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.

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 6.

Table 5. Experimental Design for Laboratory Screening – Pilot 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

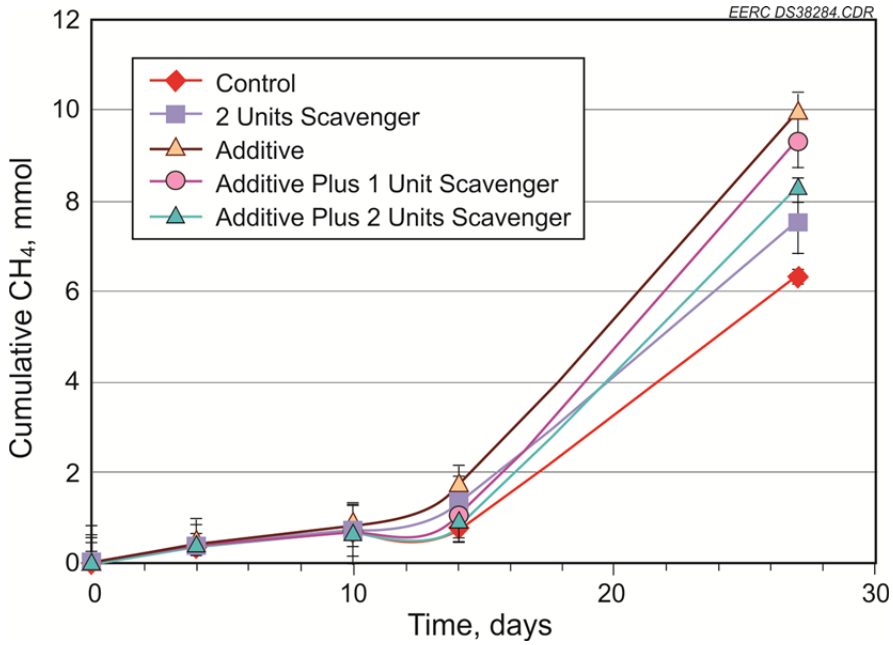


Figure 17. Effects of additive and varying scavenger dosage on methane production in serum bottles fed Haubenschild manure. The error bars represent the standard error of the triplicates. Where not shown, the error bars are within the symbols.

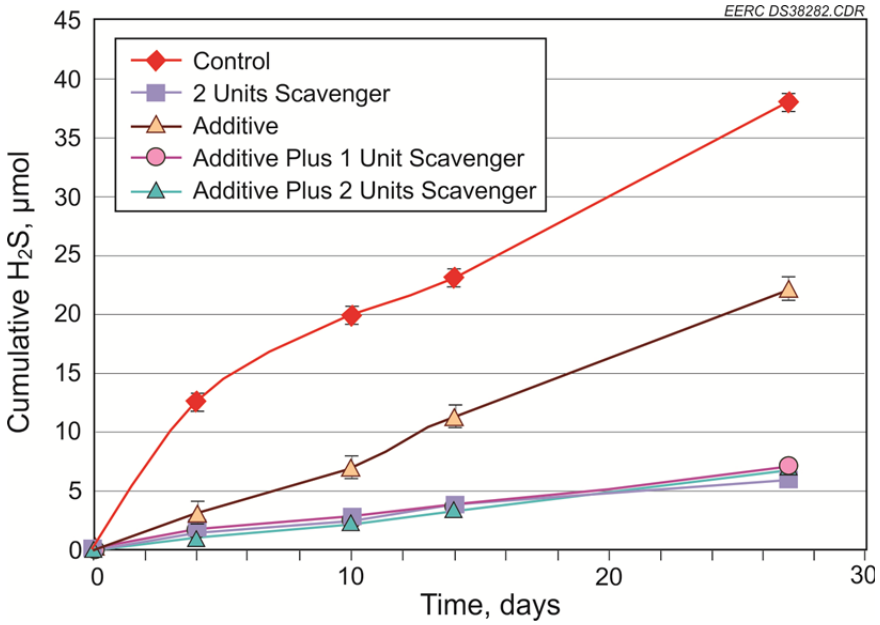


Figure 18. Effects of additive and varying scavenger dosage on hydrogen sulfide production in serum bottles fed Haubenschild manure. The error bars represent the standard error of the triplicates. Where not shown, the error bars are within the symbols.

Table 6. Experimental Design for Laboratory Screening

Condition	Fresh Manure, g	Seed, g	Additive, units of concentration	Scavenger, units of concentration
Seeded Control	36	4	0	0
Seeded Additive	36	4	0.25	0
Seeded Additive	36	4	0.5	0
Seeded Additive and Scavenger	36	4	0.25	0.5
Seeded Additive and Scavenger	36	4	0.25	1
Seeded Additive and Scavenger	36	4	0.5	0.5

The samples were periodically removed from the incubator, and 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 laboratory screening experiments are illustrated in Figures 19 and 20. Figure 19 shows cumulative methane production versus time, and Figure 20 is cumulative hydrogen sulfide versus time. After 32 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

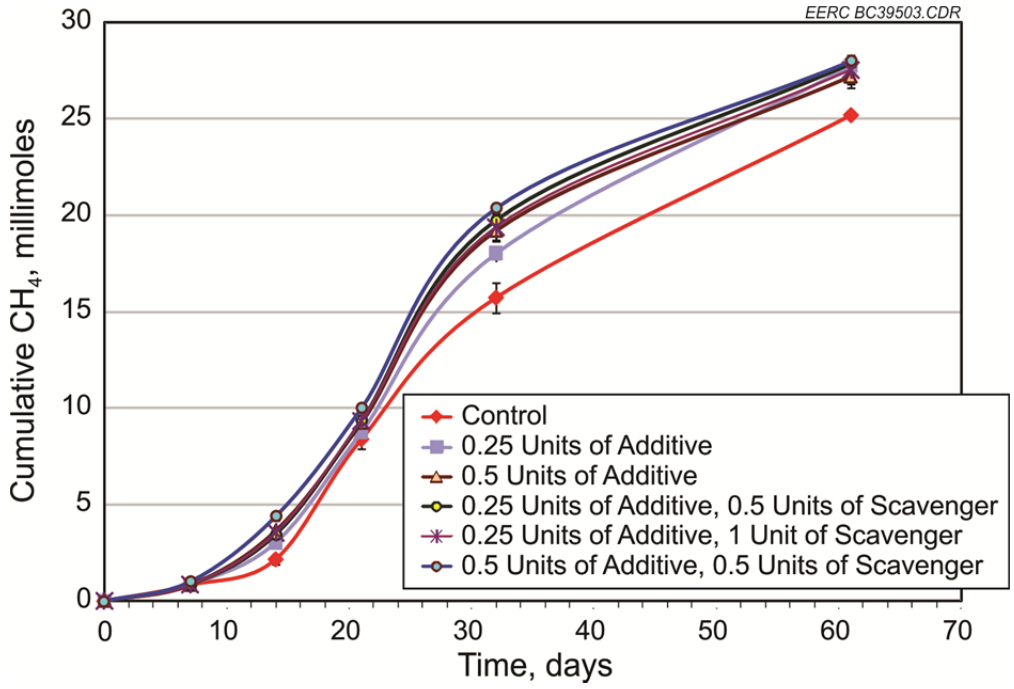


Figure 19. Effects of the scavenger and additive dosages on methane production in serum bottles fed Haubenschild manure. The error bars represent the standard error of the triplicates. Where not shown, the error bars are within the symbols.

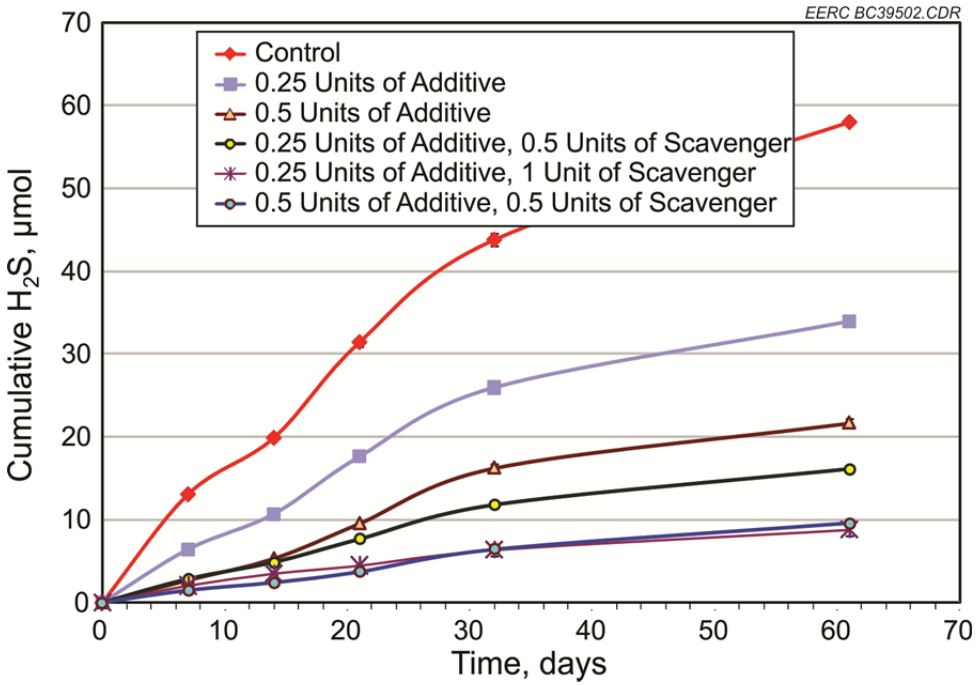


Figure 20. Effects of the scavenger and additive dosages on hydrogen sulfide production in serum bottles fed Haubenschild manure. The error bars represent the standard error of the triplicates. Where not shown, the error bars are within the symbols.

versus the control. The use of the additive and scavenger make the largest difference in the production of H_2S, with the lowest amount of H_2S formation found for the 0.25 units of additive, 1 unit of scavenger and 0.5 units of additive, and 0.5 units of scavenger conditions. The 0.25 units of additive and 0.5 units of scavenger condition provided for H_2S generation control at a low cumulative chemical addition rate. This condition was selected for use in the pilot-scale digester. Incubation and testing of these serum bottles continued through 61 days of incubation.

The conclusions after 61 days of incubation were consistent with those made after 32 days confirming the selection of the 0.25 units of additive, 1 unit of scavenger for use in the pilot-scale experiments.

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 versus the control. The use of the additive and scavenger producing the lowest amount of H_2S were found for test conditions with 0.25 units of additive, 1 unit of scavenger and 0.5 units of additive, and 0.5 units of scavenger conditions. However, because the condition with 0.25 units of additive, 0.5 units of scavenger provided good H_2S generation control at a low cumulative chemical addition rate, it was initially selected for use in the pilot-scale digester. Test conditions in the pilot digester were later increased to 0.25 units of additive and 1.0 units of scavenger.

Bench-Scale Digester Experiments

The objective of the bench-scale testing was 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 bench-scale digesters were constructed to assess the performance of the EERC additive: a control digester fed untreated manure and an experimental digester fed manure treated with the EERC additive.

Bench-Scale Digester Design, Fabrication, and Shakedown

The bench-scale digesters were configured to simulate the full-scale plug-flow anaerobic digester at the Haubenschild site in Princeton, Minnesota. The digesters were fabricated from 8-inch-i.d. Schedule 40 polyvinyl chloride (PVC) pipe. The ends of the 10-ft PVC pipes were fitted with PVC caps that were tapped and plumbed with 1-inch polypropylene ball valves installed near the bottom of each pipe end cap to accommodate feeding and removing of manure. A half-inch-diameter nipple was installed at the top of each digester, 6 inches from the outlet end, to accommodate biogas collection, measurement, and monitoring. A process diagram of the bench-scale digesters is shown in Figure 21.

Each digester has a working volume of 49 liters (13 gallons) when operating with the pipe half full. Heating is provided with recirculating hot water pumped from a water heater through half-inch-diameter tubing wrapped around the digesters. A proportional integral derivative (PID) temperature controller maintains recirculating water temperature at ±0.1°F (Figure 22). The entire digester assemblies were mounted on a frame constructed of Unistrut channel and wrapped with 1-inch-thick closed-cell foam rubber insulation (Figure 23).

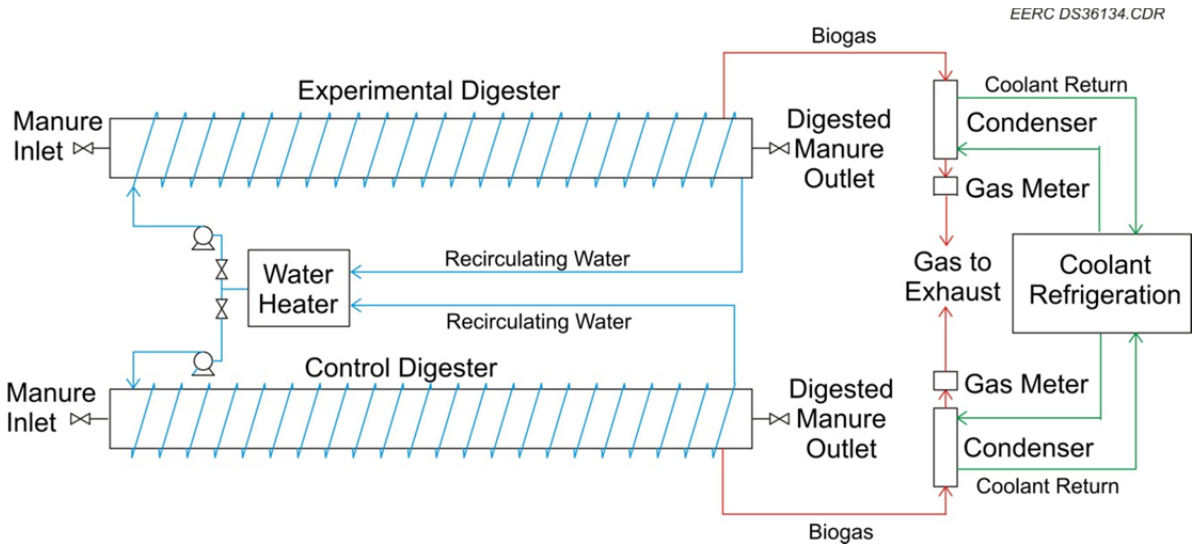


Figure 21. Bench-scale digester diagram.

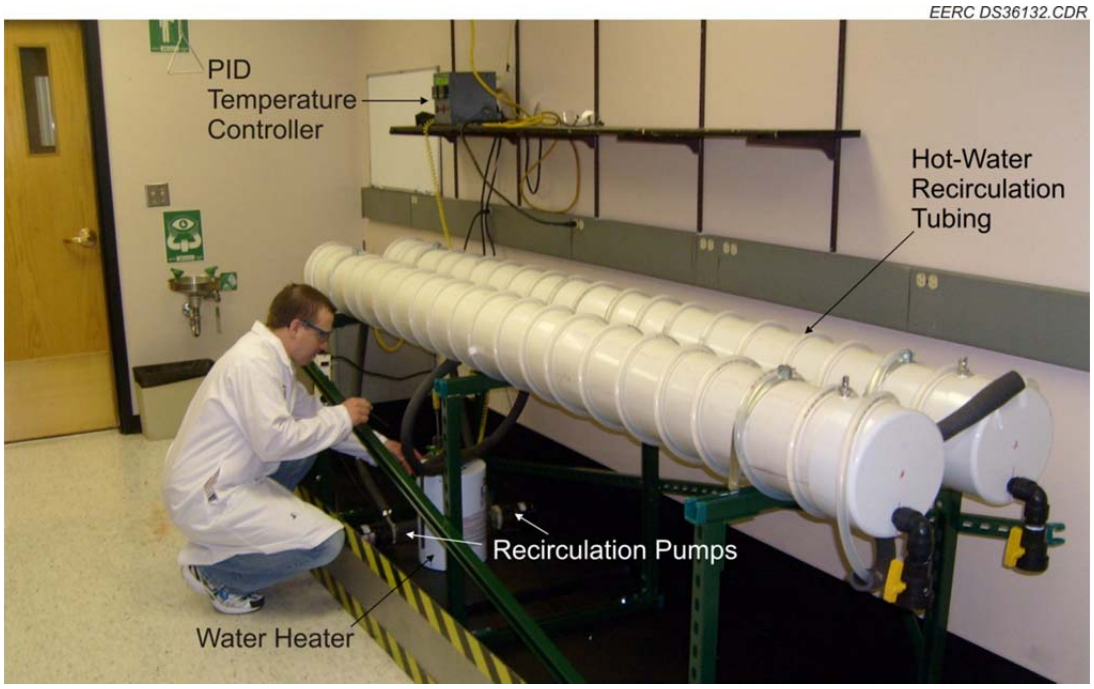


Figure 22. Bench-scale digester system under construction.

Figure 23. Closed-cell foam-insulated digesters.

Biogas from the digesters flowed to a gas-cooling system (Figure 24) which cooled the gas to a dew point of approximately 60°F to remove water vapor in the biogas prior to entering the flowmeter. The dried biogas passes through the gas meter and is exhausted to a fume hood. A 0–5-volt signal from the gas meter is routed to a signal processor, and the flow data are downloaded and saved on a dedicated computer.

The bench-scale digester system ran well during shakedown testing, with only minor difficulties, primarily leaks, which were sealed. The systems were operated for a weeklong period with the digesters filled with tap water to verify temperature control capabilities and pump performance.

Approximately 50 gallons of fresh manure and 50 gallons of digester effluent (digested manure) were collected from Haubenschild. The digested manure was used to inoculate the bench-scale digesters, and the fresh manure served as digester feed.

Bench-Scale Digester Operation and Maintenance

A digester operation and maintenance schedule was established and is presented in Table 7. 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.

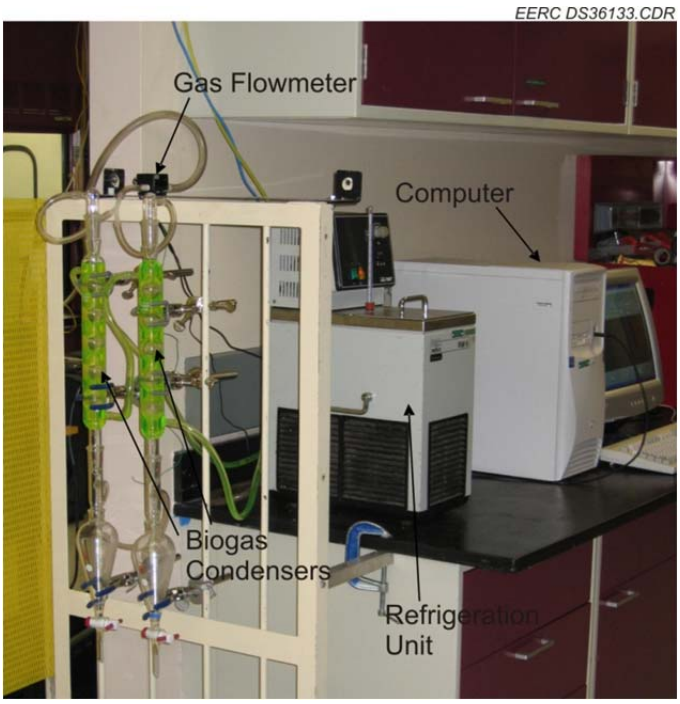


Figure 24. Biogas collection, cooling, and monitoring system.

Table 7. 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

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 were analyzed three to five times a week for the determination of methane, carbon dioxide, and hydrogen sulfide 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.

Bench-Scale Digester Testing Results and Discussion

In early October 2009, samples of both digested manure and fresh manure were collected from Haubenschild 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 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 25), a temperature difference of ±0.5°F was able to be maintained.

In mid-November 2009, after the digesters had arrived at a pseudo-steady-state operating condition, gas sampling and analysis were initiated. A fresh batch of feed manure was acquired from Haubenschild. A significant increase in H_2S in the biogas from both the control and additive digesters was noted on November 23 (Figure 26). Communication with Haubenschild 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

Figure 25. Reconfigured bench-scale digesters.

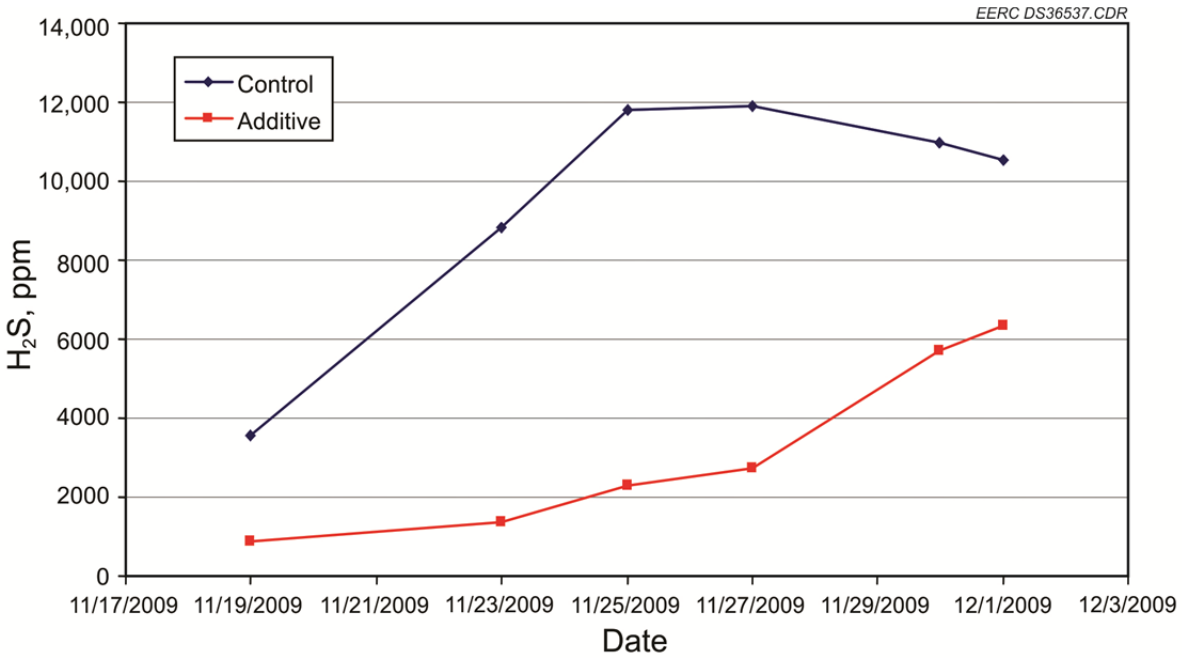


Figure 26. Bench-scale digester biogas H_2S concentration on Haubenschild manure.

ultimately gets incorporated into the digester feed manure. The result is a foreign source of SO_4 being introduced into the manure that feeds the anaerobic digester. Sulfate is a preferred electron acceptor for 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 digester and the bench-scale control digester. Examination of Haubenschild feed manure indicated the presence of gypsum particles up to 3/8-inch diameter. The use of manure from Haubenschild 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 manure feed. As seen in Figure 26, the design dose of the EERC additive was initially able to provide some level of sulfide control in the additive versus the control digester, but the higher SO_4 levels in the feed manure eventually resulted in high H_2S levels in the additive-fed digester 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 (data not shown).

The EERC contacted Riverview, located in Morris, Minnesota, and it agreed to provide manure for the project on an interim basis until Haubenschild was able to restore proper operation to its anaerobic digester. In early December, the bench-scale digesters were emptied, cleaned, and refilled with anaerobically digested manure collected from Riverview. Fresh manure was also collected from Riverview 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 27). 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.

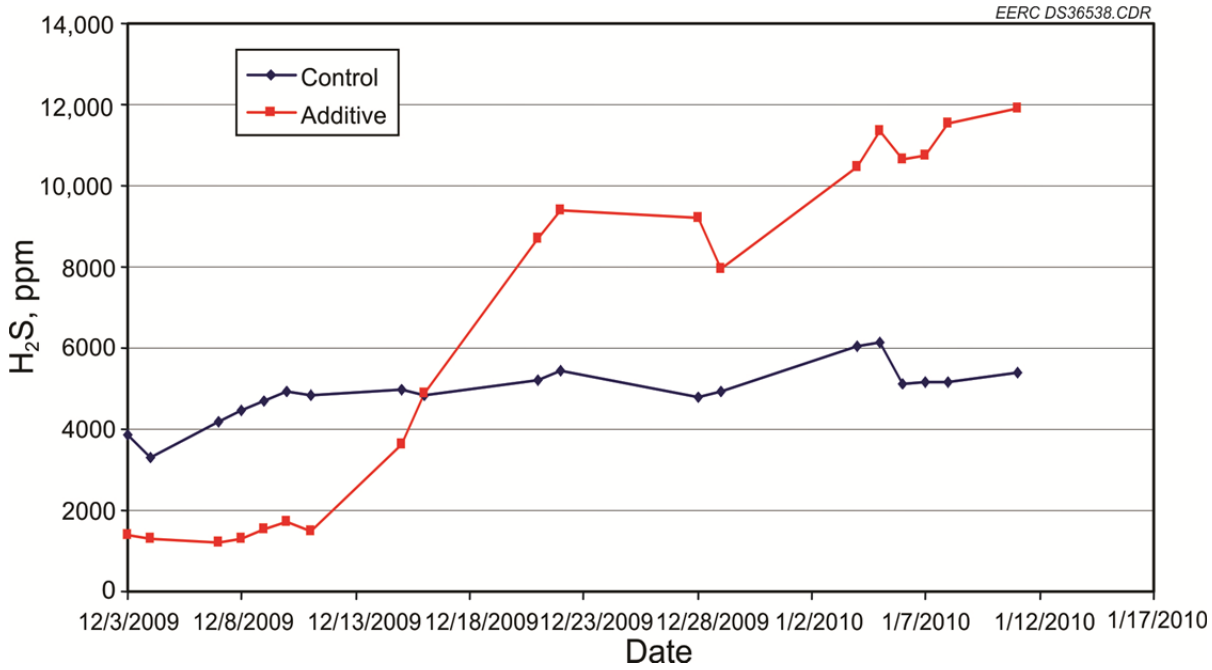


Figure 27. Bench-scale digester biogas H_2S concentration on Riverview manure.

It was assumed that all of the gypsum was not effectively removed from the additive 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.

Because of concerns about possible gas leaks and continued gypsum contamination, new control and experimental digesters were constructed. As before, each digester consists of an 8-inch-diameter by 10-foot-long PVC pipe with an operating volume of 13 gallons (49 L), a condenser for biogas moisture removal, and a continuous biogas flowmeter.

Bench-scale digester experiments were continued using manure samples collected from Riverview. Concurrent laboratory screening experiments were required to develop composition and dosage information for bench-scale digester operating conditions using the new manure. Several different operating conditions (residence time and digestate recycle) were also tested. Figures 28 and 29 illustrate the methane and H_2S gas production flow rates calculated from the average daily gas flow rate and gas composition data collected for both bench-scale plug-flow digesters. The data are given for all dates that both gas composition and flow rate data were available for both digesters. The data in Figure 28 show similar methane production rates for both digesters over the entire operating period. Variations in the observed methane production rate were associated with alterations in feed and waste rate (changes in the amount of digested sludge were made occasionally to help control the volume of material in the digesters).

The H_2S data given in Figure 29 show a similar pattern in the amount of H_2S produced in both digesters until after Day 40 when the delivery of additive at a concentration of 0.5 units was initiated in the feed to the additive digester. Prior to this day, both reactors were run under

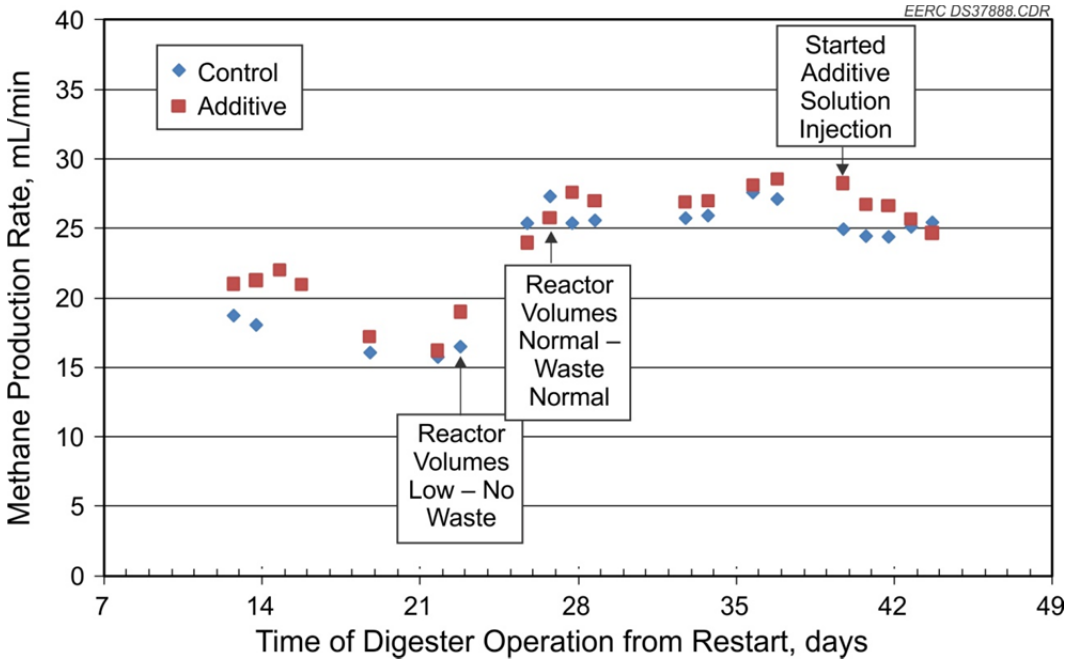


Figure 28. Methane production rate observed in the control and additive test digester fed Riverview manure.

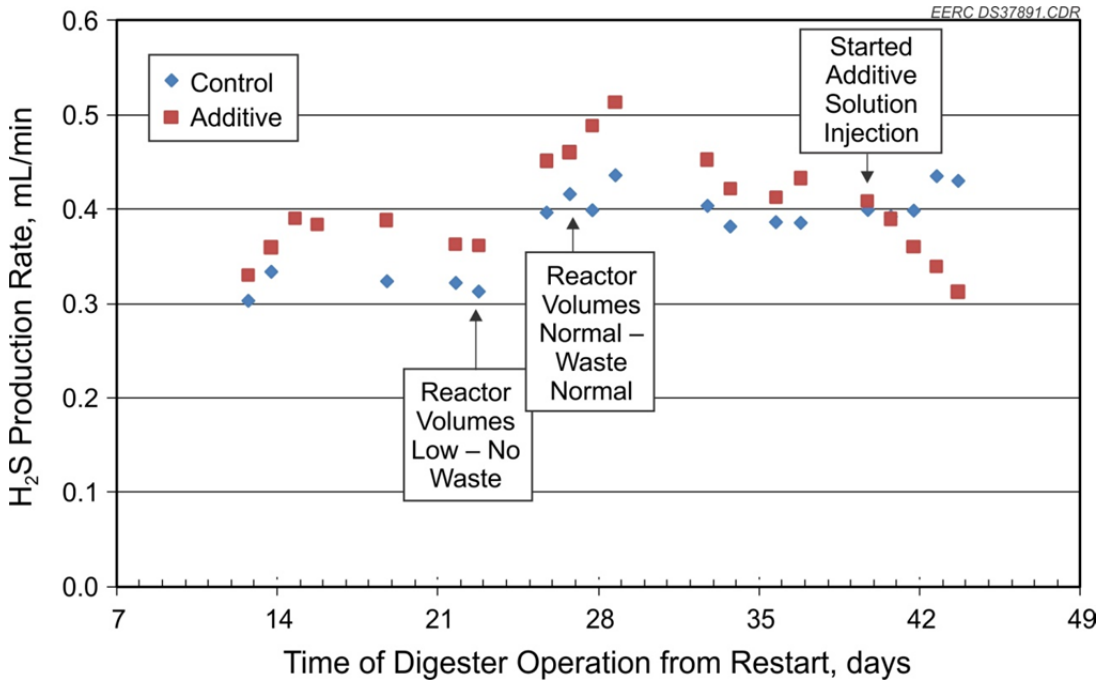


Figure 29. H_2S production rate observed in the control and additive test digester fed Riverview manure.

control conditions. Each day following initiation of scavenger addition to the feed to the reactor showed a decrease in H_2S production from the day before. With the 10-day HRT, it was expected to take at least 10 days to reach the maximum decrease in H_2S production rate – the data shown illustrate only the first 4 days of the effect of additive addition. On Day 44, the H_2S production rate in the additive feed digester was 72% of the H_2S production rate in the control digester.

Results comparing steady-state operating data from the control and experimental digesters at a 15-day residence time incorporating a 10% digestate recycle are presented in Table 8. The chemical addition to the digester feed during this period of operation included 0.5 units of additive and 2 units of scavenger.

Table 8. 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

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 using Riverview manure samples.

With continued bench-scale testing, a scum/crust layer developed in the digesters, resulting in an accumulation of solids. The accumulated crust created operational difficulty in assessing and maintaining a desired retention time. Sufficient data had been collected to warrant larger-scale testing and the bench-scale digester experiments were concluded and preparations for pilot-scale testing were initiated.

Pilot-Scale Testing

Pilot-scale digester testing was conducted using fresh manure samples on-site at Haubenschild. Pilot testing was supplemented by additional laboratory screening experiments that were necessary to verify appropriate doses of EERC additive–scavenger combinations for the new manure.

Pilot Digester Design, Fabrication, and Installation

A pilot-scale digester system was designed and fabricated at the EERC. Shown during construction in Figure 30, the digester system consists of a 24-inch-diameter, 20-foot-long insulated PVC test vessel having a total volume of 470 gallons (1779 liters) and a nominal

Figure 30. Photograph of pilot-scale anaerobic digester vessel during construction.

operating volume (half full) of 235 gallons (889 liters). The reactor contains two heat-transfer pipes (stainless steel tubing), one that is a loop that enters and exits through the manure inlet end bulkhead and the other a straight piece of tubing that passes the full length of the vessel approximately 4 inches from the reactor bottom. The straight piece of heat-transfer tubing is used to maintain the reactor temperature near the temperature set point of 35°C (95°F), and the inlet loop heat-transfer tubing is used to bring the temperature of freshly added manure up to the set point temperature after it has been added to the reactor (daily).

A computer data acquisition and control system was developed to allow for collection of gas flow rate, reactor mass, and reactor temperature data and for control of valves used to deliver hot water to the reactor for the purpose of temperature control. A screen shot of the user interface for the data acquisition and control system is in Figure 31. The mass of manure in the digester was monitored using three load cells mounted below the reactor. Biogas was directed through a condensing heat exchanger to remove the moisture before the dry biogas was directed through a mass flowmeter for quantifying measurement of the biogas production rate. The waste biogas was then combined with the flow from the full-scale digester and burned in the dairy's genset engine.

The digester system was transported to Haubenschild, unloaded (Figure 32), and installed in the generator building at the dairy (Figure 33). The digester contents were 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 was connected to and supplied from Haubenschild's digester system.

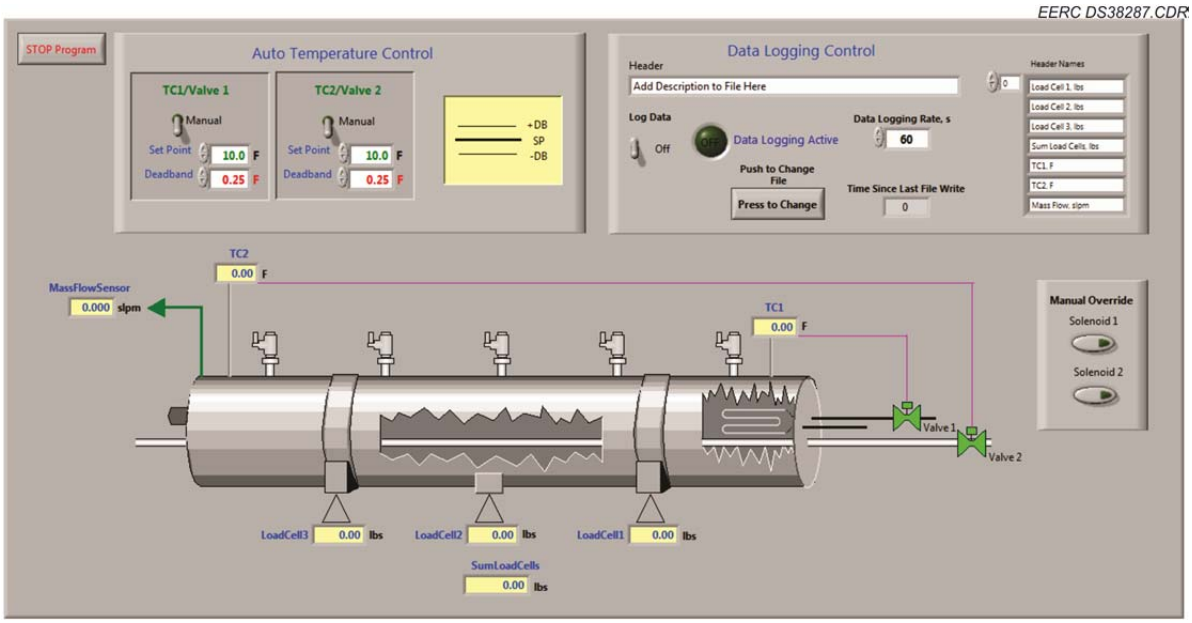


Figure 31. Pilot-scale anaerobic digester data acquisition interface

Figure 32. Photograph of pilot-scale anaerobic digester vessel during installation. The full-scale digester is visible in the background.

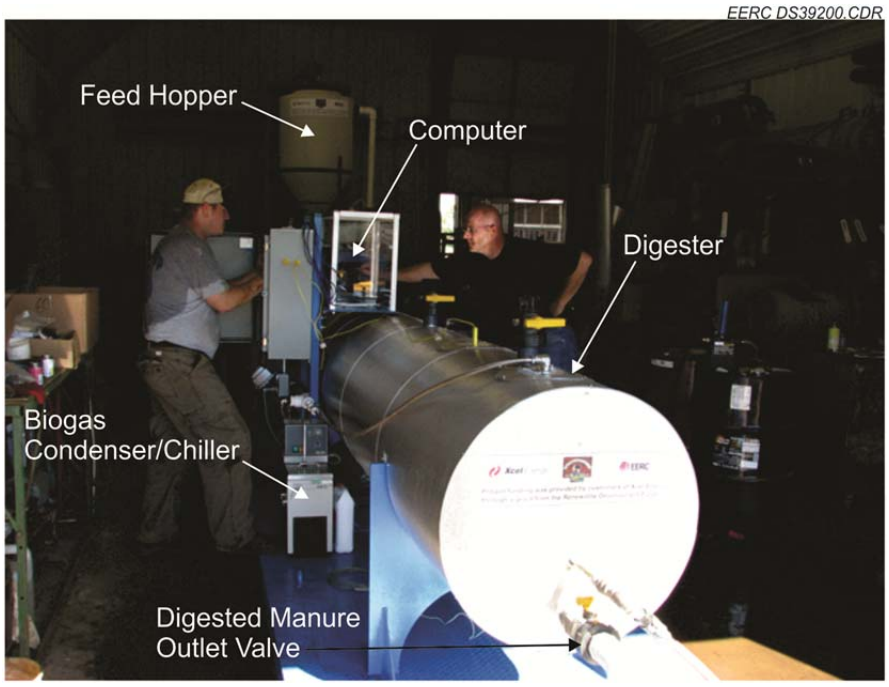


Figure 33. Photograph of digester installed in the generator building at Haubenschild. The raw manure feed hopper is in the background. The foreground shows the effluent end of the digester.

Pilot Digester Operation

The pilot-scale digester was operated for 98 days from start-up on August 13, 2010, through shutdown on November 19, 2010. The full-scale digester was fully operational during this entire time period. During this time period, the pilot-scale digester was operated using three different additive plus scavenger conditions: from start-up until September 23, 2010 (41 days), the manure was supplemented with a very low concentration (0.1 units) of scavenger (no additive). This can be considered a baseline condition in which little to no change in H_2S production from that of the full-scale digester would be expected. During the 34-day period from September 23, 2010, through October 25, 2010, the manure was supplemented with additive at 0.25 units of concentration and scavenger at 0.5 units of concentration, a dosing condition established by the laboratory screening experiments. On October 26, 2010, the scavenger concentration used was doubled to 1.0 units of concentration while keeping the additive concentration at 0.25 units. The 0.25 units of additive concentration, 1.0 units of scavenger concentration condition was used for feeding the reactor for 24 days through the last day of feeding on November 18, 2010. This increase in scavenger concentration was deemed necessary because although the H_2S concentration in the biogas from the pilot-scale digester had decreased from the values observed for the full-scale digester, the concentration had leveled off at a value exceeding the desire to control production to very low levels. Additionally, the results from the final serum bottle experiments confirmed that the 0.25 units of additive, 1.0 units of scavenger condition should provide greater control of H_2S production (at a low increase in chemical cost).

Daily operation of the digester proceeded as follows. Fresh manure from a collection pit at the farm was fed to the pilot digester daily, coinciding with feeding cycles of the full-scale digester. During the early morning feeding of fresh manure to the full-scale digester, farm personnel routed approximately 15 gallons (i.e., slightly exceeding the feed volume needed) of this manure to the pilot digester feed hopper. EERC employees arrived at the farm during or soon after this operation, turn on the feed hopper mixer to homogenize the sample, and wasted the excess fresh manure. A sample of this wasted manure was used for measurement of fresh manure pH and for determining total (TS) and VS concentrations. After the volume of manure in the feed hopper has been reduced to 12 gallons, the scavengers were added (as a high-concentration stock solution) and mixed with the manure for a minimum of 10 minutes. Once the scavenger was well mixed into the manure, the additive was added (as a high-concentration stock solution) and the contents of the hopper mixed for an additional 10 minutes. On occasion, the fresh manure sample had such high solids concentrations that the motor for the hopper mixer was not capable of turning the impeller shaft (insufficient torque), and late in the period of operation the mixer motor failed. Operators then mixed the hopper contents my hand with a wooden paddle for a minimum of 10 minutes and until the operator felt the hopper contents were reasonably homogeneous. Once the scavenger and additive had been added and mixed into the manure, a sample was taken for measurement of the pH of the mixture to ensure that addition of the scavenger and additive did not cause a large change in pH. Feeding of the mixture of fresh manure, additive, and scavenger was performed after gas composition data collection steps were completed.

After feeding was completed and the mass of the digester noted, a volume of approximately 12 gallons of digested manure is removed through a valve at the end of the digester. A sample of the digested manure is collected for measurements of pH, TS, and VS.

Biogas was routed from the digester through a condenser/chiller to remove moisture before being directed to the mass flowmeter. Gas production rate and digester mass are measured continuously, and the data were reduced to daily average values. Gas composition was measured occasionally by gas chromatography. Gas samples were collected in 1-liter tedlar bags and transported by EERC personnel or shipped overnight to the EERC for analysis. On-site analysis of gas samples for H_2S was initiated on September 28, 2010, using Kitagawa tubes, which have a detection range of 50 to 2000 ppm H_2S. The analysis method involves the use of a syringe-type pump to pull a known volume of gas through a glass tube containing a reactive chemical which changes color upon reaction with H_2S. The tubes are calibrated and provide a measure of the amount of H_2S in the gas sample.

Digester temperature, mass, and gas flow were monitored continuously via the computer data logger. Routine daily operations include adding feed manure and removing an appropriate volume of digested manure and measuring and recording pH of feed and digested manure samples. Total VS of the feed and digested manure were analyzed three times a week. Digester biogas samples were collected approximately weekly for analysis at the EERC. Kitagawa tube analysis of H_2S concentrations was performed approximately three times a week from September, 28 2010, through the end of the project.

The pilot digester was initially operated with a very low addition rate of scavenger. This provided a period of operation consistent with operation as a control digester. Near the end of this reporting period (after the 32-day serum bottle test results were obtained), operation was switched to test conditions that consist of the addition of EERC additive and scavenger to all of the manure fed to the digester. Biogas samples were analyzed weekly during acclimation periods and daily during steady-state operation for the determination of CH_4, CO_2, and H_2S content. Alkalinity of the manure was also measured periodically.

Digester Test Results

Figure 34 illustrates pilot digester temperature as measured by the two temperature control thermocouples and by manual thermometer measurements of digester effluent. The target operating temperature was 95°F. During the initial operating period, it was impossible to operate at the 95°C temperature because of high ambient temperatures (high outdoor temperatures and heat from the genset located in the same building). Table 9 presents the mean, standard deviation about the mean, minimum, maximum, and median temperature data, which are shown graphically in Figure 34. The averages for the control thermocouples were higher than those for the manual measurements, but none of these averages was statistically different (greater than one standard deviation) from the target value of 95°F. The lowest average daily temperatures were observed on days when power outages at the farm led to a lack of availability of hot water for use in regulating the digester temperature. Typically, there was no discernable upset in digester operation. However, in one instance, November 14, 2010, a winter storm caused a power outage that resulted in a temperature drop in both the pilot-scale and full-scale digesters. The gas production rate for the full-scale digester subsequently decreased sufficiently to result in a shutdown of the genset. A corresponding reduction in biogas production by the pilot-scale

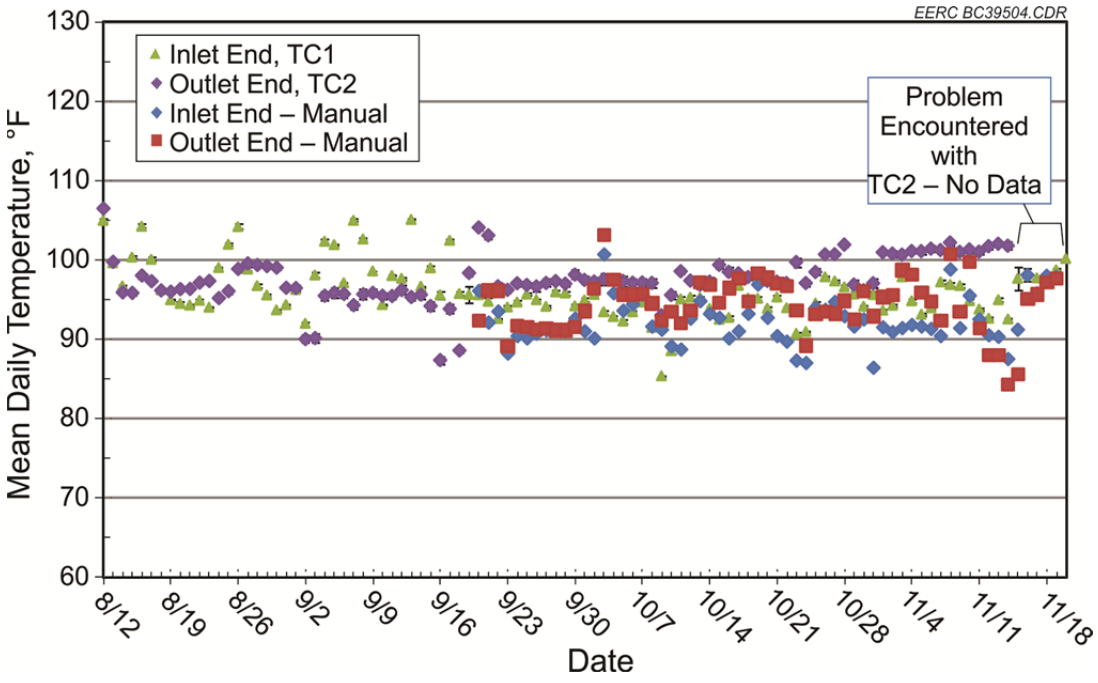


Figure 34. Pilot-scale digester temperature. Error bars represent ±1 95% confidence interval of the daily mean.

digester was apparent but difficult to quantify because of a failure of the feed inlet gate valve on the digester, which created a leak sufficient to prevent accurate gas production rates. In addition, the power outage led to the condensation in the biogas line and mass flow sensor, which led to the malfunction and failure of the flowmeter.

Figure 35 illustrates the total mass of the operating digester. The nominal operating mass is approximately 1300 kg. From August 12, 2010, to September 30, 2010, the mass was maintained within 5% of this value, with a total average daily value ranging between 1234 and 1370 kg. Near the end of that time, the digester exhibited a relatively rapid increase in mass. Over the

Table 9. Average (mean), Minimum, Maximum, Median Temperatures of the Pilot-Scale Digester

	TC1, inlet	Manual Inlet Temp., °F	TC2, outlet	Manual Outlet Temp., °F
Average	96.1	92.3	97.6	94.2
Std. Dev.*	3.4	3.0	3.0	3.5
Minimum	85.3	86.4	87.3	84.3
Maximum	105.1	100.7	106.5	103.1
Median	95.5	91.6	97.2	94.7

* Standard deviation.

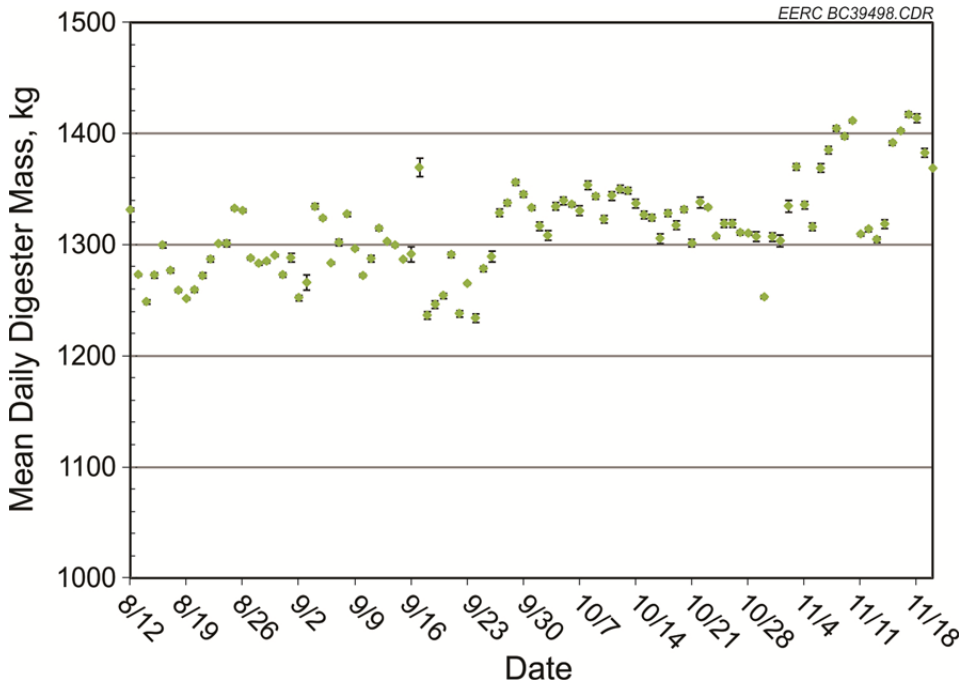


Figure 35. Mean daily digester mass. Error bars represent ±1 95% confidence interval of the daily mean.

operating period from October 1 to November 19, the mass of the digester varied between 1237 and 1453 kg, with a mean of 1317 ±48 kg. The maximum value during this period was 11.8% greater than the target. Solids accumulation was attributed to the higher solids content of the feed manure (as high as 12% on some days) and the nature of plug-flow digester operation.

Figure 36 illustrates the mean biogas production rate for the pilot-scale digester. The expected nominal flow rate based on the lab-scale digester was 1.5 slpm (standard liters per minute). Initially, the flow rate was less than that level because the digester began operation on digested solids from the full-scale digester. A high rate of variability was observed during initial feeding operations and was attributed to daily ambient temperature variations that were warmer than the target operating temperature, which affected the microbial population dynamics. The period from August 29 to September 23 was considered steady-state operation under control conditions. The corresponding gas flow rate was 1.36 ±0.13 slpm. The first day of the EERC additive and scavenger addition was September 24. The data appear to suggest a gas flow rate increase from steady-state control conditions to a 7-day moving average of close to 1.5 slpm. On October 17, the average was observed to decrease to around 1.2 slpm. Behavior of the system as noted by the operators indicated the likely presence of a slow and/or intermittent leak or leaks. Efforts were made to find and seal all possible leaks with limited success, and it was observed that on certain days, it was difficult to measure gas flow after closing reactor valves after feeding operations. A failure of the mass flowmeter occurred on November 12. Attempts were made to measure gas flow with a rotameter with limited success. A persistent leak did not allow sufficient pressure to build up for accurate gas flow determinations using a rotameter, which operates at higher differential pressure than the mass flowmeter.

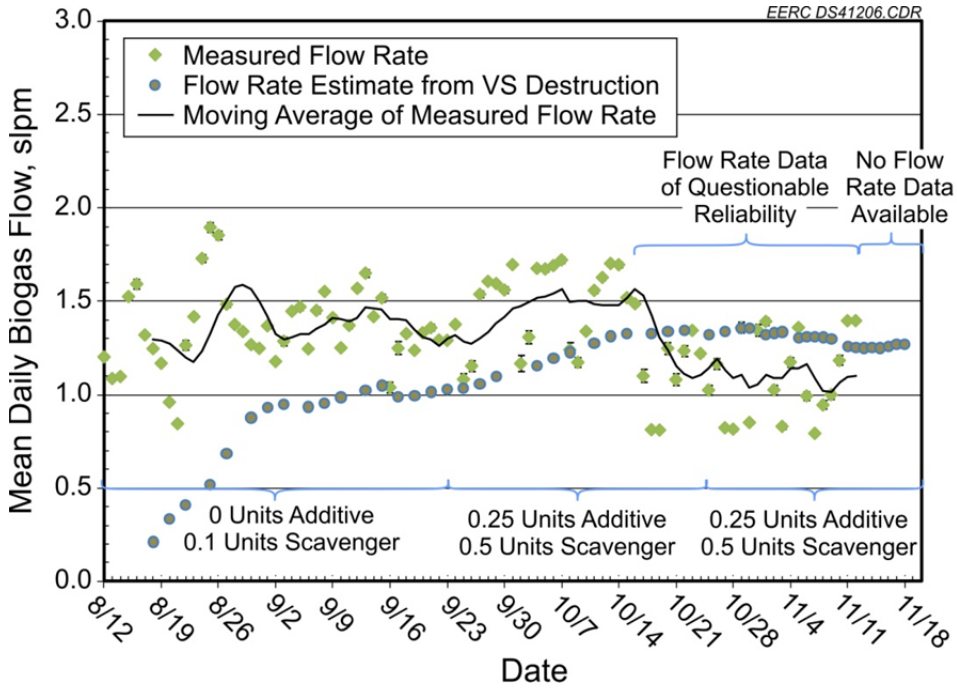


Figure 36. Mean daily biogas flow. Error bars represent ±1 95% confidence interval of the daily mean. The trend line provided is the 7-day moving average. Filled circles represent the flow rate estimated from VS destruction data presented later.

A final set of data points presented in Figure 36 were obtained by calculating the biogas production rate from VS destruction data presented later (Figure 43) while assuming 0.7 m^3 of methane production/kg of VS destroyed and a methane concentration of 60%. These data presented as gray circles in Figure 36 support the assertions that the step change reduction in gas flow rate observed from the flow rate measurement equipment was caused by a leak rather than a change in the health of the digester and that good gas production was maintained until the digester was shut down. Figure 37 illustrates biogas methane content for both the pilot-scale and full-scale digesters. The values from both digesters are essentially equivalent, with the average value for the pilot digester being 59.1% and for the full-scale digester 59.9%.

Figure 38 illustrates hydrogen sulfide content for both the pilot-scale and full-scale digesters. Two sets of analytical data are shown for each digester. The data sets labeled as Haubenschild Digester and EERC Pilot Digester are results of gas chromatography, while the data sets labeled EERC Kitagawa and Haubenschild Kitagawa were collected on-site using Kitagawa tubes. It appears that the Kitagawa tube analyses tended to underestimate H_2S concentrations but were nonetheless effective at providing confirmation of the general trend of H_2S generation.

The timing of the observed decreases in H_2S concentration for the pilot-scale digester confirms the efficacy of using the EERC additive and scavenger. The first decrease in H_2S from between 1620 and 2080 ppm to levels between 1200 and 1430 ppm occurred sometime between 10 and 15 days following the addition of 0.5 units of additive and 0.25 units of scavenger to the pilot-

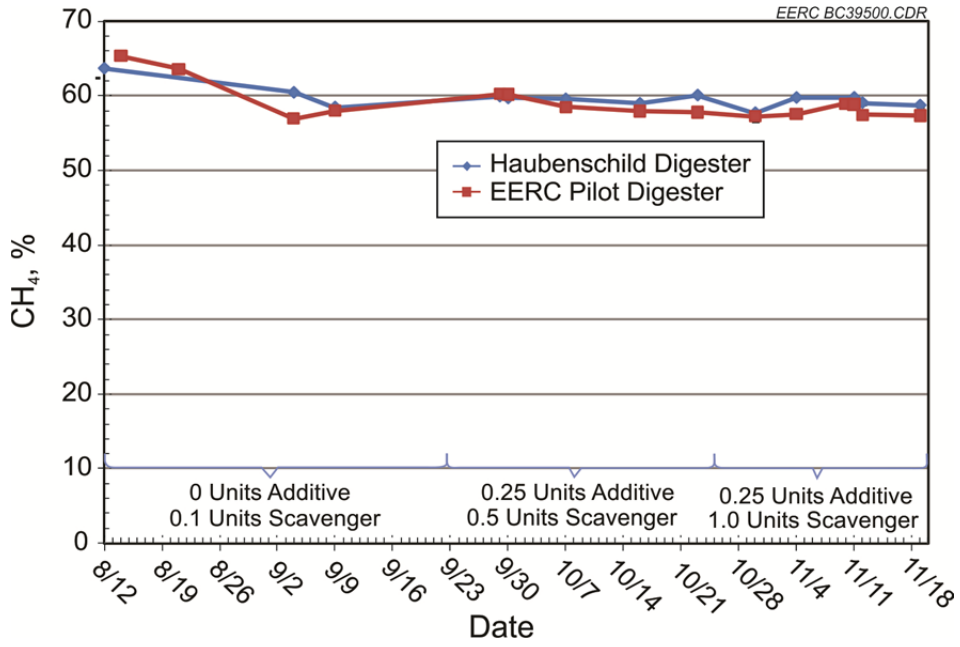


Figure 37. Methane concentration in full-scale (Haubenschild) and pilot-scale (EERC) digesters. Error bars based on ±1 standard deviation are not visible because they are smaller than the size of the symbol.

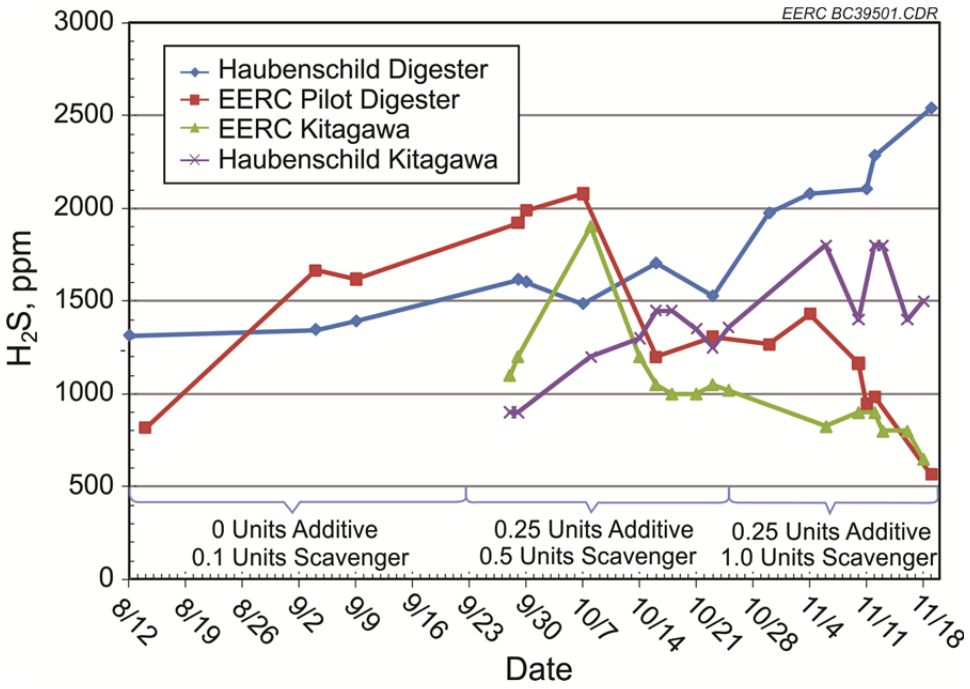


Figure 38. Hydrogen sulfide concentration in full-scale (Hubenschild) and pilot-scale (EERC) digesters. Error bars of ±1 standard deviation for the gas chromatography data (blue diamond and red square) are not visible because they are smaller than the size of the symbol.

scale digester feed manure. The second decrease from the 1200–1430-ppm range to the 565-ppm (and, apparently, still decreasing) value started between 10 and 15 days, following the increase in scavenger concentration to 1.0 units. This behavior is consistent with the results from the serum bottle experiments (Figure 20), which revealed the 0.25 units of additive, 1.0 units of scavenger condition provided better control of H_2S production than the 0.25 units of additive, 0.5 units of scavenger condition.

pH and Alkalinity

The pH of the feed to the pilot-scale reactor was within the range of 6.74 to 7.35 throughout the course of the study. The minimum pH observed was that for raw manure on the first day of reactor operation, August 13, 2010. The pH of the reactor influent slowly increased throughout the period of reactor operation, with a maximum value of 7.35 observed on the final day of reactor feeding, November 17, 2010. The lower raw manure pH values during the earlier period of digester operation were most likely due to higher ambient temperatures. Higher microbial activity is expected at higher ambient temperatures, which would lead to increased acidification of the raw manure in the raw manure collection sump. Effluent pH from the digester showed a decreasing trend, with the effluent pH values observed to be as high as 7.92 during the first week of pilot digester operation and as low as 7.54 during the final week of digester operation. All of these pH values fall within a safe range for maintenance of effective digestion.

Figure 39 shows an expanded view of the final 25 days of reactor operation during which the pilot-scale digester was supplemented with 0.25 units of additive and 1.0 units of scavenger. The data are shown for this period because it is during this period that the greatest potential existed for differences in the pH of the pilot digester from those for the full-scale digester because of the higher chemical addition rates. The data clearly indicate that the pH of the pilot-scale reactor feed is slightly lower (average pH of 7.12 ± 0.15) than the raw manure pH (average pH of 7.27 ± 0.13). This decrease in pH upon chemical addition was expected. The 0.15 pH unit decrease is reasonable and acceptable.

The data in Figure 39 also show the effluent pH values for both the pilot- and full-scale digesters. From October 25 through November 14 the pH in both reactors was virtually identical, 7.57 ± 0.02 versus 7.60 ± 0.04, respectively, for the pilot-scale digester versus the full-scale digester. During the period from November 15 through November 19, the full-scale digester samples indicate a higher pH but the pilot-scale digester pH remains the same. The reason for the increased pH in the full-scale digester is unknown.

It should be noted, because both the pilot- and full-scale digester operate as plug-flow systems with residence times of close to 20 days, the effluent pH would not be immediately influenced by changes to the influent. Therefore, the rise in influent pH at the end of the study should not cause the observed increase in pH of the full-scale reactor effluent. More importantly, the lack of an apparent drop in effluent pH for the pilot-scale digester indicates the decreased influent pH resulting from chemical addition did not negatively impact the pH in the digester.

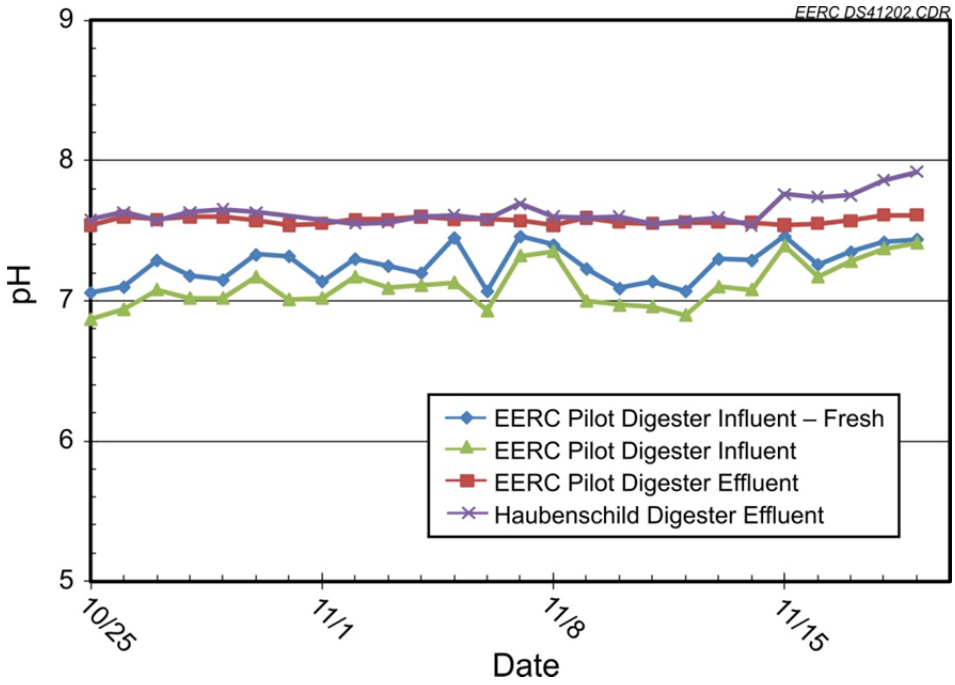


Figure 39. pH of the pilot- and full-scale digester during the final operation period. "EERC Pilot Digester Influent – Fresh" represents the influent pH of the manure fed to the full-scale digester; "EERC Pilot Digester Influent" represents the pH of the manure after addition of scavenger and additive and represents the pH of the material feed to the pilot-scale digester. All pH values fall within a safe range for maintenance of effective digestion.

Alkalinity measurements were performed on select samples. The original plan had been to perform these titrations more frequently, but the results obtained from the samples that were analyzed indicated it was not necessary to do this. Samples collected on September 17, 2010, and October 22, 2010, illustrate this fact. The pilot digester feed and effluent samples collected on September 17, 2010, had alkalinities of 14,400 and 16,800 mg/L as $CaCO_3$, respectively. Raw manure (full-scale digester feed), pilot digester feed, pilot digester effluent, and full-scale digester effluent samples collected on October 22, 2010, were found to have alkalinities of 13,800, 12,400, 14,000, and 15,000 mg/L as $CaCO_3$, respectively. These alkalinity concentrations were sufficiently high to indicate it was not necessary to perform alkalinity titrations on a regular basis.

Total and Volatile Solids

Figures 40 and 41 show the results of TS and VS measurements performed during operation of the pilot-scale digesters. Complete data sets are available for the fresh manure (full-scale influent) and effluent from the pilot-scale digester. A full data set is available for the full-scale digester for the final operating period. A partial data set for the pilot-scale digester influent (measured after addition of the scavenger and additive) indicates it is reasonable to use the fresh manure values as the influent concentration for both the full-scale and pilot-scale digester.

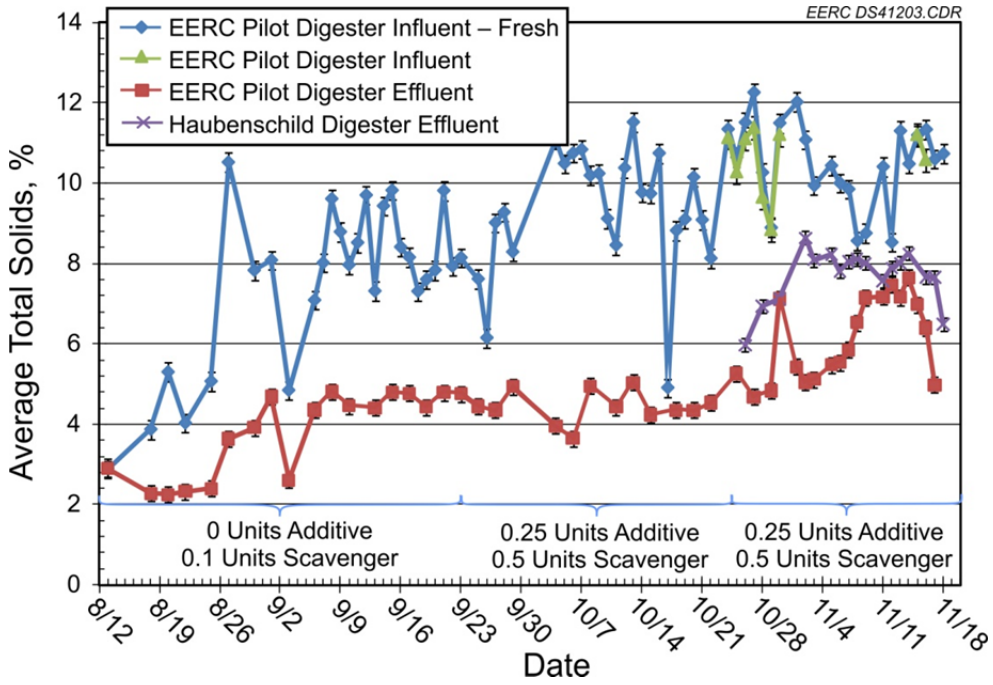


Figure 40. TS concentration versus time for pilot-scale and full-scale digesters.

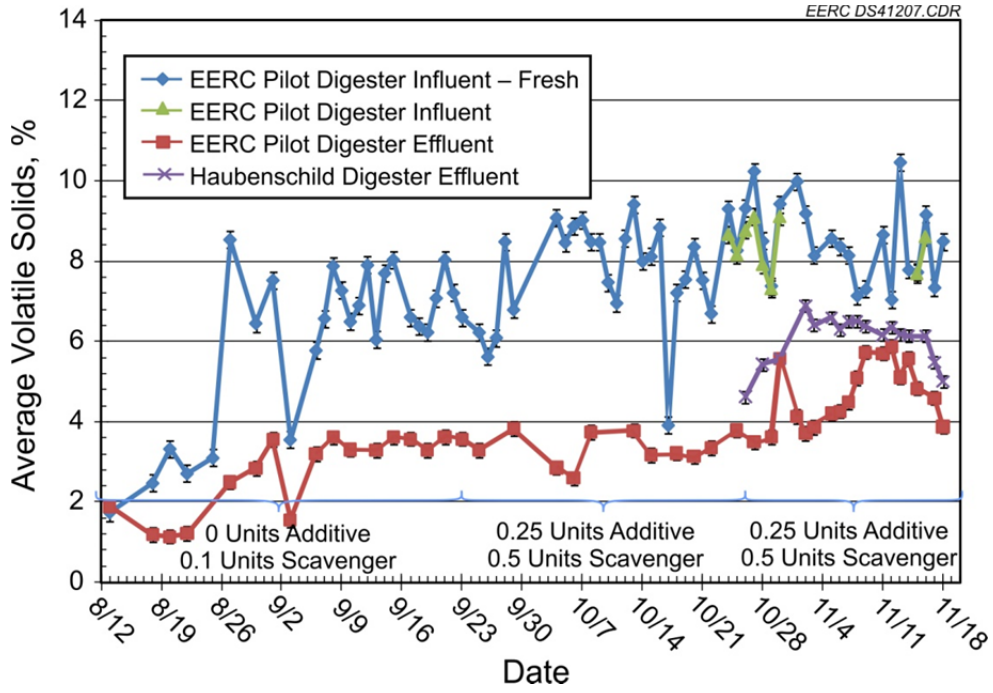


Figure 41. VS concentration versus time for pilot-scale and full-scale digesters.

From Figures 40 and 41, it appears that greater TS and VS destruction was observed for the pilot-scale digester than for the full-scale digester. This may be true to some extent, but the pilot digester was also observed to have been accumulating solids (see Figure 35), so the results presented here may be somewhat misleading. The conclusion best derived from the data is that addition of the scavenger and additive may have led to greater VS destruction which would have also led to greater amounts of biogas production, but insufficient data are available to be sure.

Because the reactors are plug-flow and the influent solids concentrations are highly variable, it is not reasonable to compare the effluent solids concentration to the feed solids concentration from any given day in order to calculate the % TS or %VS destruction, as this would lead to very high values on days with high solids concentrations in the influent and low and even negative values for days with low solids concentrations in the influent. However, sufficient data exist for the pilot-scale digester to allow for calculation of the average % solids destruction by calculating the cumulative solids loading to the reactor and the cumulative solids removal from the reactor. The cumulative TS and VS fed and wasted from the pilot-scale digester are shown in Figure 42. The cumulative solids data shown in Figure 42 were used to calculate the percent TS and VS destruction data shown in Figure 43. From Figure 43 it appears that VS destruction typically ranged from 52% to 59%, with TS destruction ranging from 45% to 50%. Final cumulative influent VS were 80% of influent TS. Final cumulative wasted VS were 70% of wasted TS.

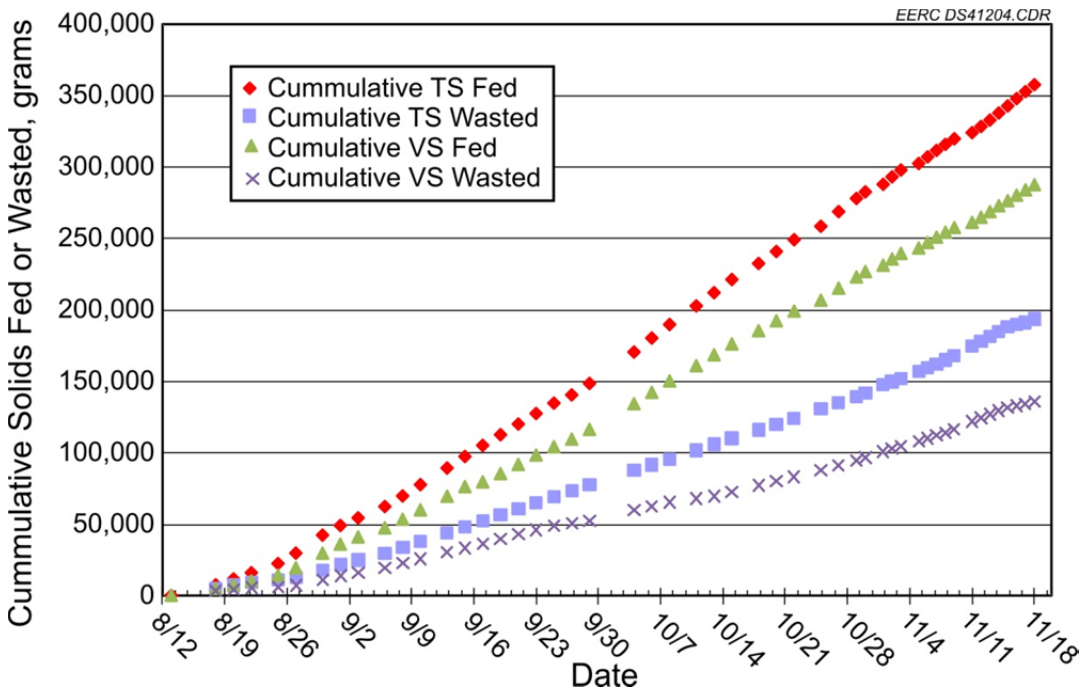


Figure 42. Cumulative amount of solids fed and wasted from the pilot-scale digester.

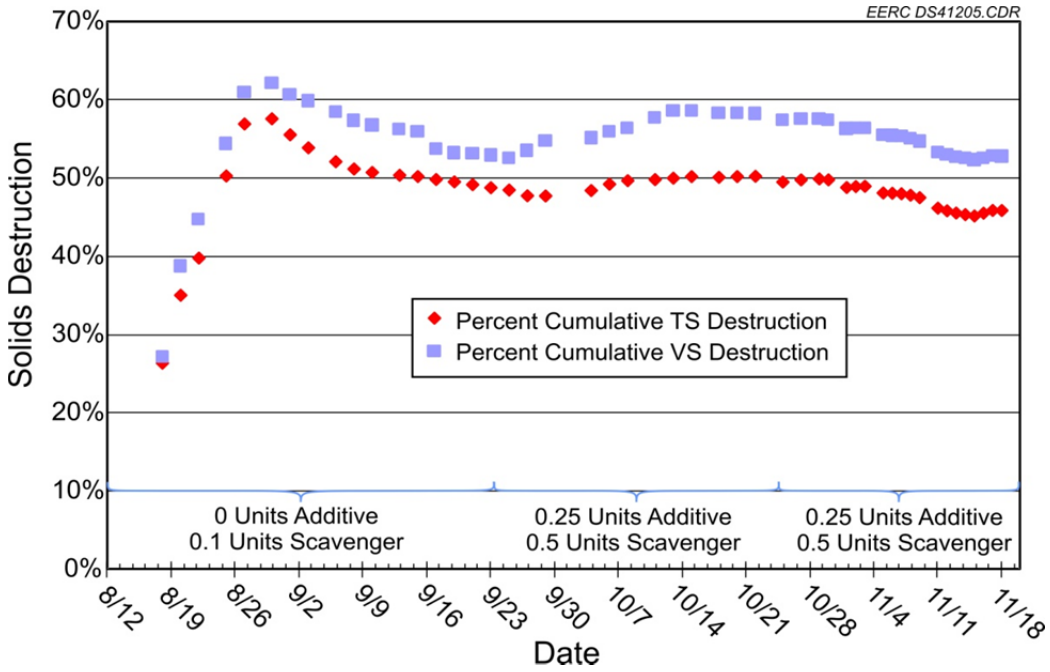


Figure 43. Percent TS and VS destruction calculated from cumulative amount of solids fed and wasted from the pilot-scale digester.

Because solids accumulated in the pilot digester, it is possible to make a calculated correction to the final solids destruction. From visual observation of the data in Figure 35, we assumed that the accumulated mass in the reactor could be taken as 100 kg. Of this 100 kg, no more than 10 kg of the accumulated weight would have likely been TS (8 kg of VS) if we use the apparent average influent concentration from Figure 41 and the influent average VS content of 80% of the TS concentration (i.e., ignore solids destruction and any effects of solids settling based accumulation that may have occurred). Based on this, we can calculate that there may have been an accumulation of as much as 10 kg of total and 8 kg of VS. Correcting for the accumulation of solids in the reactor would change the final point shown in Figure 43 from 45.8% to 43.1% cumulative TS destruction and 52.8% to 50.0% for cumulative VS destruction. We consider this

a relatively minor error in the observed performance that may have resulted for not accounting for daily changes in the mass of solids in the reactor during the solids destruction calculations.

Conclusions from the Pilot-Scale Experiments

The pilot-scale studies provided clear evidence that the use of a mixture of EERC additive and scavenger to Haubenschild manure is effective at reducing the concentration of H_2S in the produced biogas. The formulation containing 0.25 units of additive and 0.5 units of scavenger appeared to be capable of producing only a moderate reduction (perhaps 30% to 50%) in the H_2S concentration, leaving close to 1000 ppmv. Increasing the scavenger concentration of 1 unit while maintaining the additive at 0.25 units provided additional control down to close to 500 ppmv, which was 20% to 25% of the H_2S concentration seen in the biogas from the full-scale digester at that time.

The improvement in performance of the pilot-scale digester based on changes in chemical feed formulation was consistent with the results observed from the serum bottle screening study run using manure from Haubenschild. This justified the decision to perform the pilot-scale tests despite the problems encountered during bench-scale testing, where significant problems were encountered in digester operation and there were inconsistencies between serum bottle screening study results and the performance of the bench-scale reactor. It is possible the problems with the bench-scale studies were the difference in manure source (Riverview vs. Haubenschild), but they may have also been because of the material flow problems encountered as a result of the small diameter of the bench-scale reactors.

Economic Assessment

Potential Market

In 2011, EPA AgStar estimated 541 million kWh of electricity generation from 176 digesters across the United States This project utilized dairy manure, an abundant renewable resource in Minnesota. According to U.S. Department of Agriculture (USDA) census data (2007) Minnesota had over 5000 farms representing nearly 460,000 milk cows. While AgStar estimates that a dairy should have 500 cows to provide an economically viable digester project, it does note a number of variables that could make smaller projects more practical, including utility rates, codigestion opportunities, and farm energy use. For example, Jer-Lindy Farms, near Sauk Center, Minnesota, operates an anaerobic digester on a farm with fewer than 200 cows. The electricity produced from an internal combustion engine connected to a 40-kW generator is used on the farm to power the digester and pumps and to offset electrical use at the dairy. A significant additional benefit to the digester is odor control (Schmidt, 2011). Minnesota has 400 dairy operations that have more than 200 cows, which includes a total of over 223,000 cows (U.S. Department of Agriculture, 2007). While manure production depends on a number of factors, including the type of cow (jersey, holstein, etc.), body size, and diet, typical manure production for 200 cows is considered to be 24,100 lb/day (U.S. Environmental Protection Agency, 2012). The manure generated by those cows represents nearly 27 million pounds/day of a renewable resource that could provide a significant market opportunity for electricity production using anaerobic digestion and, subsequently, for H_2S control.

Cost Comparison to Natural Gas Price

A cost analysis was performed to evaluate the cost of applying additive and scavenger to the full-scale Haubenschild digester. Bulk chemical pricing of technical-grade additive and scavenger was obtained from several suppliers. The price used in the calculation was the lowest-cost FOB (freight on board) price quoted for a U.S. supplier. Historic data on chemical costs were found sporadically, but the costs to produce the additive have remained relatively stable over time. The cost of supplying these chemicals for H_2S control was reduced to a cost per MMBtu (million Btu) of biogas. This is compared to the equivalent cost of the same amount of natural gas based on the futures market price of natural gas on April 19, 2011. Table 10 contains key assumptions related to biogas production and the equivalent cost of natural gas needed to supply the same amount of energy.

Table 10. Assumptions Used in the Cost Analysis

Full-Scale Digester Volume (Haubenschild)	500,000 gallons
Hydraulic Retention Time	20 days
Daily Feed	25,000 gallons/day
Daily Biogas Production	72,500 cf/day
Methane Content of Biogas	60%
Btu Content of Biogas	600 Btu/cf
Biogas Energy Available	15,877.50 MMBtu/year
Btu Content of Natural Gas (range is 800–1200)	1000 Btu/cf
Price of Natural Gas [a]	4.247 $/MMBtu
Cost to Buy Natural Gas	65,097.75 $/year

[a] www.bloomberg.com/markets/commodities/futures/ – price as of April 19, 2011.

Table 11 provides details concerning the daily and yearly chemical cost needed to apply the use of the EERC additive and scavenger for the purpose of H_2S control at Haubenschild Farms. It indicates that the equivalent cost of the chemicals is $9.15 to $10.41 per MMBtu of biogas produced, depending on the control solution used. This is 2.15 to 2.45 times the cost of the equivalent energy content of natural gas at current commodities market natural gas prices. It should be noted that natural gas prices are highly variable over time, and the actual cost to a given customer is typically significantly higher than the commodities market price. The Energy Information Administration reported that in 2009 the average price of natural gas delivered to U.S. electric power consumers was between $6.00 and $6.99 per 1000 cf. Prices paid by commercial and residential consumers in the United States are shown in Figures 44 and 45.

In short, although natural gas prices in Minnesota are among the highest in the nation, the cost of chemicals to achieve a desired sulfide control level during the anaerobic digestion of dairy manure is economically prohibitive. Given that natural gas prices could fluctuate considerably or that a premium price could be put on distributed renewable energy, the cost of the chemicals coupled with biogas power production could become economical in the future.

Cost Comparison to Alternative Biogas Treatment Techniques

The costs for use of the additive and scavenger were also compared to the cost of using various alternative methods of biogas treatment to remove hydrogen sulfide. The costs of the EERC additive were compared to five established technologies which included the addition of metal ions, removal with iron oxides, adsorption onto activated carbons, wet scrubbers, and biological processes. Although several publications discussed the technical and economic aspects of each of these technologies, the cost information and comparison methodology was adapted from Chen et al. (2010).

Table 11. Chemical Costs Associated with the EERC Additive and Scavenger

Additive Concentration, units	0.25	0.25
Scavenger Concentration, units	0.5	1
Total Cost to Treat Feed, $/day	397.95	452.71
Total Cost to Treat Feed, $/year	145,250.64	165,240.45
Cost to Treat Digester, $/MMBtu – compare to natural gas price	9.15	10.41

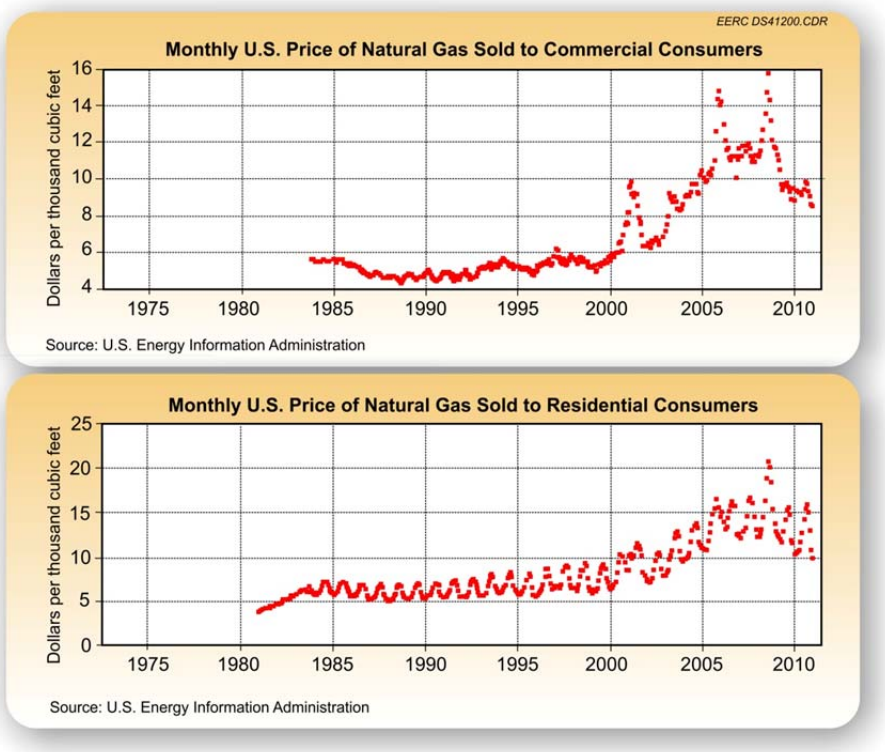
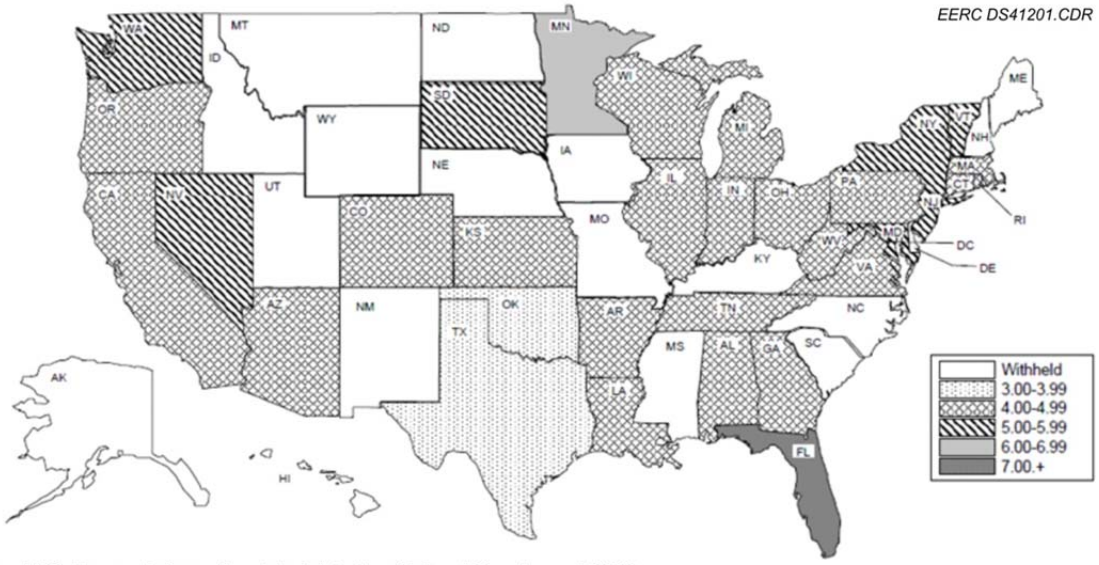


Figure 44. Historic natural gas prices in the United States.



Source: U.S. Energy Information Administration/Natural Gas Annual 2009

Note: Prices are in nominal dollars; for DC, HI, and ND, electrical price is not applicable.
Source: U.S. Federal Energy Regulatory Commission (FERC) Form 423. Monthly Report of Cost and Quality of the Electric Plants.

Note: At 1000 Btu/cf, the price per thousand cubic feet is equivalent to the price per MMBtu.

Figure 45. Average price of natural gas delivered to U.S. electric power consumers, 2009 (dollars per thousand cubic feet).

Iron sponge

Iron sponge is a term used to describe a class of technologies that utilize iron oxides or iron hydroxides to convert H_2S to iron sulfide. The reaction takes place in a vessel containing iron oxide-impregnated media (typically wood chips).

Biofilter

A biofilter is a biological treatment method for sulfide removal. Biofilter technologies utilize packed vessels containing a variety of growth media on which cultures of sulide-oxiding bacteria (Thiobacillus) convert H_2S to sulfate. Methanotrophs (methane-consuming bacteria) can also inhabit a biofilter which could result in a reduction of the methane content of the biogas.

Iron chloride injection

The use of iron chloride involves either placing the iron chloride directly into the digester or in a mixing tank prior to the digester or by passing the biogas through an iron chloride solution. The iron chloride reacts with the H_2S to form iron sulfide salts.

Impregnated activated carbon

Activated carbons can be used to remove H_2S in biogas. These activated carbons can be impregnated with a variety of compounds, including sodium bicarbonate, sodium carbonate, sodium hydroxide, potassium hydroxide, potassium iodide, and potassium permanganate. However, potassium hydroxide is a common compound used for sulfide removal.

Wet scrubber

In wet scrubber processes, the biogas is delivered countercurrent to an aqueous solution of either sodium hydroxide or sodium hypochlorite in a packed column. When the NaOH is used, the reaction forms Na_2S, and when NaOCl is used, the reaction produces NaCl and Na_2SO_4.

To provide an economic comparison of the respective technologies, available cost and production data were converted to an equivalent-cost-per-1000-ft^3 basis according to the following equation, which assumed a 20-year project lifetime:

$$\text{Cost of Treatment} = [(\text{CapEx}/20\text{ years})+(\text{Annual O\&M})]/[(\text{Biogas Production})\times(365)]\times 1000$$

Calculated treatment costs on a \$/1000-ft^3 basis are presented in Table 12. As illustrated in the data, the EERC additive–scavenger combination for the treatment of dairy manure digester biogas was not the least costly alternative and was only less expensive than iron chloride injection. Potassium hydroxide-impregnated activated carbon appears to be the least-cost alternative.

Table 12. Relative Costs of Sulfide Removal Technologies

Technology	Capital Cost, $	Annual O&M[1] Costs, $/yr	Biogas Production, ft^3/day	Cost of Biogas Treatment, $/1000 ft^3
EERC Additive/Scavenger (0.25 units additive, 1.0 unit scavenger)	50,000	165,000	72,500	6.37
Iron Oxide (Sulfur Rite)	43,600	23,800	47,800	1.49
Biofilter	22,300	3930	7420	1.86
Iron Chloride Injection	12,800	29,300	3530	23.24
KOH-Activated Carbon	50,000	5440	47,800	0.46
Wet Scrubbers	28,100	4500	7420	2.18

[1] Operating and maintenance.

The cost of sulfide removal depends on a number of factors, including the source of the biogas (manure digesters, landfills, wastewater treatment plants, etc.), biogas production rate, concentration of sulfide in the biogas, and level of sulfide removal achieved. Where available, cost data in terms of cost per unit of sulfide removed were collected or estimated and are presented in Table 13. It should be noted, however, that these data were derived from different anaerobic systems, each producing a different biogas composition at different rates.

These data, as such, are not directly comparable and are intended to give the reader a rough estimate of removal costs. Each of the technologies compared, however, was reportedly capable of greater than 75% removal of sulfide from the respective biogas stream. The EERC additive–scavenger technology, represents the highest-cost alternative in terms of $/lb of sulfide removed. This demonstrates that dairy cow manure is not the most economical application for this

Table 13. Relative Costs of Sulfide Removal Based on Cost Per Unit of Sulfide Removed

Technology	Cost for Sulfide Removal, $/lb
EERC Additive/Scavenger (0.25 units additive, 1.0 unit scavenger)	34.59
Iron Oxides	3.61–3.86[a]
KOH-Activated Carbon	0.80–0.91[a]
KOH-Activated Carbon	5.45[b]
Na_2CO_3-Activated Carbon	9.09[b]
Iron Oxide (Sulfur Rite)	3.00[c]
Iron Sponge	0.16–0.71[a]
Liquid Triazine Absorption	8–10[d]

[a] Zicari, 2003.
[b] Abatzoglou and Boivin, 2008.
[c] Heguy and Bogner, 2011.
[d] Compton et al., 2012.

technology. A better application for renewable energy production would be the anaerobictreatment of high-strength wastewaters, such as those associated with potato-processing plants, sugar beet refineries, and ethanol plants. In liquids, the EERC additive gets uniformly distributed in the water, providing intimate contact of the additive with sulfate-reducing bacteria. The enhanced level of contact results in the desired "kill" effect which, ultimately, prevents the formation of H_2S and alleviates the need for a scavenger material, reducing the overall cost of treatment.

Summary of Economics

A summary of work performed to assess and compare the economics of using the proprietary EERC hydrogen sulfide-removing additives and scavenger process in relation to other removal technologies is as follows:

- Although natural gas prices in Minnesota are among the highest in the nation, the cost of the EERC additive to achieve a desired sulfide control level during the anaerobic digestion of dairy manure is economically prohibitive.

- Given that natural gas prices could fluctuate considerably or that a premium price could be put on distributed renewable energy, the cost of the EERC additive coupled with biogas power production could become economical in the future.

- Various alternative methods of biogas treatment to remove hydrogen sulfide were compared to the costs of the EERC additive, including the addition of metal ions, removal with iron oxides, adsorption onto activated carbons, wet scrubbers, and biological processes.

- The EERC additive achieved 80% removal of hydrogen sulfide and all of the alternative methods purportedly can achieve a removal of 75% or more of the hydrogen sulfide.

- The EERC additive–scavenger technology, represents the highest-cost alternative in terms of $/lb of sulfide removed.

- At least for dairy cow manure, the EERC sulfide or sulfur removal technology is not the most economical application. A better application for renewable energy production might be the anaerobic treatment of high-strength wastewaters, such as those associated with potato-processing plants, sugar beet refineries, and ethanol plants.

Project Benefits: The following benefits have been derived based on research and development work performed under this project:

The project demonstrates that anaerobic digestion of biomass is an attractive distributed power option in the Xcel Energy territory. Distributed energy generally refers to smaller energy generation systems as compared to large base load and centrally located energy generation. Digesters such as the plug-flow systems demonstrated in this project can take advantage of

smaller quantities of biomass resources, thereby producing valuable renewable energy (and possible credits), which is mandated in the Xcel Energy electrical power distribution system. A technology was demonstrated that produces a fuel gas from biomass residues for combined heat and power (CHP) applications that could generate up to 250 kW of power per system. With respect to dairy manure systems alone, the focus of this project, potentially 400 such distributed power systems could generate power in Minnesota alone.

- The project demonstrated the viability of clean methane (CH_4) production using an anaerobic digestion process that also minimizes the waste disposal costs of, in this case, manure or other vegetative or food-processing biomass wastes. Renewable methane produces renewable electricity when burned in an internal combustion engine generator.

- The project shows the potential for increasing renewable energy production and reducing greenhouse gas emissions in the Xcel Energy territory. Anaerobic digester technology essentially captures methane, a potent greenhouse gas, and converts it to renewable energy and CO_2. This project provides the benefit of potentially encouraging digester technology development which would add to the 55,000 metric tons of methane or 1.2 million metric tons of equivalent CO_2 that is already being reduced by digestion systems across the United States.

- Anaerobic digestion technology as demonstrated by this project provides the benefit of odor control, the production of a stabilized biosolid product suitable for use as bedding material or soil amendments, and a nutrient-rich liquid product that can be used as fertilizer. Without these secondary benefits, small-scale renewable energy production from digester systems would not be possible.

- This project specifically provided a benefit to dairy manure digester technology development by focusing on reducing the amount of hydrogen sulfide in the digester produced gas. A high degree of sulfide control was shown through the use of a proprietary additive that selectively kills sulfate-reducing bacteria (SRB), the root cause of sulfide production, combined with a scavenger that provides further reductions in the concentration of hydrogen sulfide (H_2S) in the biogas. The project also showed a potential to produce additional methane which, in turn, can produce additional electricity. H_2S is a toxic gas that contributes to foul odors and causes problems with power generation equipment. When combusted, H_2S is oxidized to SO_2, which may be present at levels that can exceed air quality standards. Bench- and pilot-scale testing of a proprietary additive yielded a hydrogen sulfide reduction of up to 80% (and corresponding SO_2 emission reduction when the biogas is combusted). Reduced SO_2 in combustion exhaust reduces equipment corrosion and promotes the reduction of regional haze.

- A technical benefit of this project included the development of successful bench- and pilot-scale testing protocols that can be replicated by other engineers and digester experts for advancing superior systems. Tests were conducted in two laboratory plug-flow reactors using both Haubenschild Farms and Riverview Dairy manures. Results

were precise for gas production, microbiology maintenance, and system monitoring, making for a very adaptable bench-scale system. This differentiating experimental setup gave rapid and well instrumented results and, again, is of great benefit to the research community as an example test system that can derive scalable results rather than relying totally on a large-scale real-world digester which is more time-consuming and costly.

- Laboratory-scale testing revealed the benefit of a successful additive system and manure digestion scenario for a demonstrated 46% reduction in biogas sulfide concentration and a 20% increase in methane generation rate.

- A 910-liter on-site anaerobic digester test facility was operated for 100 days at the Haubenschild farm, providing a great benefit to Minnesota and the anaerobic research community as a demonstrated robust test system configuration that can be mimicked by other researchers. Even though the system experienced challenges because of early-winter severe weather and manure quality inconsistencies, the system showed excellent sensitivity to daily differences in manure character, and manure moisture content on additive performance.

- Another benefit from the large pilot-scale test facility work at Haubenschild Farm Dairy was a greater than a 75% reduction in biogas sulfide content compared to data from the full-scale digester. The only downside was that no significant difference in biogas methane concentration was noted during pilot testing.

- A significant benefit was the conversion of manure-derived methane to CO_2, effectively reducing the carbon footprint of a future system incorporating this system by at least 50%. Manure was effectively reduced to gas and peatlike cellulose; with the gas fraction consisting of methane, carbon dioxide, and some minor H_2S and NO_x. Although not within the scope of this project, internal engine combustion of this 50%–75% methane, 25%–45% carbon dioxide, and <10% NO_x and water–gas mixture would effectively produce an exhaust gas of 95%+ carbon dioxide, with some minor amounts of NO_x. This effectively reduces the carbon footprint of a typical cow manure dairy (if all manure consumed in a digester) by 45%.

- A great benefit from this work was a best-attempt economic assessment given the nature of the research project and short time line for results. The economic assessment suggested that, while effective in controlling sulfide generation in the anaerobic digestion of dairy manure, the additive was not as cost-effective as commercial postdigestion biogas treatment techniques. These economic constraints may be overcome if the biogas produced during anaerobic digestion was able to be converted into a higher-value end product such as ammonia fertilizer. The project was able to secure additional funding to conduct a complementary project that demonstrated the potential to utilize the biogas from anaerobic digestion to produce hydrogen and ammonia, two high-value products. The hydrogen can be used in fuel cells to produce electricity, while the ammonia is a farm commodity that is directly utilized in farming. Given the relatively low cost of electricity in Minnesota, the production of ammonia at

reasonable cost would provide an economic benefit to the anaerobic digestion of dairy manure.

- Finally, a potential benefit from this work is that other industries within the Xcel Energy territory may be impacted with an even greater return. Higher-energy-density feedstocks, including hog manure and high-strength agricultural processing wastewaters from facilities such as sugar beet-, potato-, meat-, and poultry-processing plants in Minnesota, are capable of producing more energy than dairy manure. More importantly, wastewaters also provide a more favorable media for using the EERC additive. The ability of the EERC additive to achieve optimal control requires intimate contact of the additive with SRB. The ability to uniformly distribute the additive in waters should reduce the need for higher application rates of the EERC additive and the need to use sulfide-scavenging agents associated with manure digesters. The potential application toward these industries in Minnesota alone could double the number of potential distributed renewable energy generation systems.

Project Lessons Learned: The project successfully demonstrated a high degree of sulfide control through the use of an additive that selectively kills SRB, the root cause of sulfide production, combined with a scavenger that provides further reductions in the concentration of H_2S in the biogas. The project also showed a potential to produce additional methane which, in turn, can produce additional electricity. While sulfide control during manure digestion was demonstrated, the chemical costs associated with applying the additive and scavenger on a continuous basis were found to be economically prohibitive for the enhancement of dairy manure digestion projects compared to other commercially available sulfide removal techniques. It is possible that chemical addition during times of high sulfate loading to a digester could be an economically feasible way to avoid anaerobic digestion inhibition effects and process upsets due to spikes in H_2S generation, but detailed investigation of this potential application was beyond the scope of this project. The project successfully demonstrated that sulfide control using an additive to selectively kill SRB and prevent the formation of sulfide during anaerobic digestion is technically feasible. This control may also be achieved with a slight enhancement in methane production, but that increase in methane was not universally demonstrated.

While not originally proposed or planned, the project conducted testing on manure samples from two different dairies. Differences in farm/dairy operations appeared to have a significant influence on the character of the manure and, subsequently, a difference in digester performance along with differences in biogas quality. Different additive formulations were required to provide the best sulfide control for the respective manures. This is important in that the additive/scavenger formulation would have to be custom-tailored for each application or farm.

In general, it is probable that heterogeneities in dairy cow manure and the use of a digester without mechanical mixing in this project (and commonly used for manure digestion) appear to provide for microenvironments within a digester where SRB experience less exposure to the additive. This led to the need to use higher additive concentrations than originally anticipated based on past work in order to get significant H_2S control. The higher H_2S concentrations were partially controlled by the use of a scavenger. The proposed importance of microenvironments is derived from general knowledge of how biofilms and microenvironments protect

microorganisms from toxic and inhibitory effects in other waste treatment applications, from disinfection efforts in water treatment and distribution and from success with using the additive for H_2S control during previous work with high-strength wastewater applications where the additive is evenly distributed in wastewater.

With manures, a higher concentration of additive and a scavenging agent to bind the sulfide that was produced are necessary to achieve a high degree of sulfide control. The need for higher additive concentrations and the use of scavenger increases the cost of chemicals for sulfide control. For the additive and scavenger application rate needed for H_2S control at Haubenschild (based on the pilot study results), the total cost of chemicals exceeded the cost of purchasing natural gas with energy content equivalent to the biomass that is produced by the full-scale digester. The chemicals costs also exceed the annual cost of operating several commercially available biogas treatment systems.

While the biogas generated from anaerobic digestion of dairy manure is typically used to produce heat and electrical power, the conduct of this project revealed that dairies of a certain size (1000 cows) produce more electricity than is needed by the dairy operation. The excess electricity can be sold to the electrical utility at less than retail prices, often at a price that does not justify the overall expense of operating the anaerobic digestion/CHP facility system. The use of the biogas to produce a higher-value product such as hydrogen or ammonia may be justified if that higher-value product can be produced at a reasonable cost.

Usefulness of Project Findings: A key finding of this research is that sulfide control using additives to selectively kill SRB is not likely a cost-effective technique during the anaerobic digestion of dairy manure. Further, any biomass feed material to an anaerobic digester where an additive cannot be uniformly distributed throughout the media would likely require higher application rates of the additive plus the use of a scavenging agent to remove the sulfide that is produced. The additional costs of more additive chemicals and the scavenging chemicals will likely render this approach uneconomical for manure applications.

Further, dairy manure itself provides a relatively low-energy feedstock for anaerobic digesters. Figure 46 illustrates the relative biogas potential from different biomass substrates showing the potential of cow manure to other materials.

Higher-energy-density feedstocks, including hog manure and high-strength agricultural processing wastewaters from facilities such as sugar beet-, potato-, meat-, and poultry-processing plants in Minnesota, are capable of producing more energy than dairy manure. More importantly, wastewaters also provide a more favorable media for using the EERC additive. The ability of the EERC additive to achieve optimal control requires intimate contact of the additive with SRB. The ability to uniformly distribute the additive in waters should reduce the need for higher application rates of the EERC additive and the need to use sulfide-scavenging agents associated with manures. The ability to evenly distribute the additive throughout a given media provides the needed contact between the additive and SRB to result in the desired kill effect. If enhanced methane production is realized through the application of the EERC additive, as was observed in bench-scale testing, additional electricity generation is possible at no additional cost.

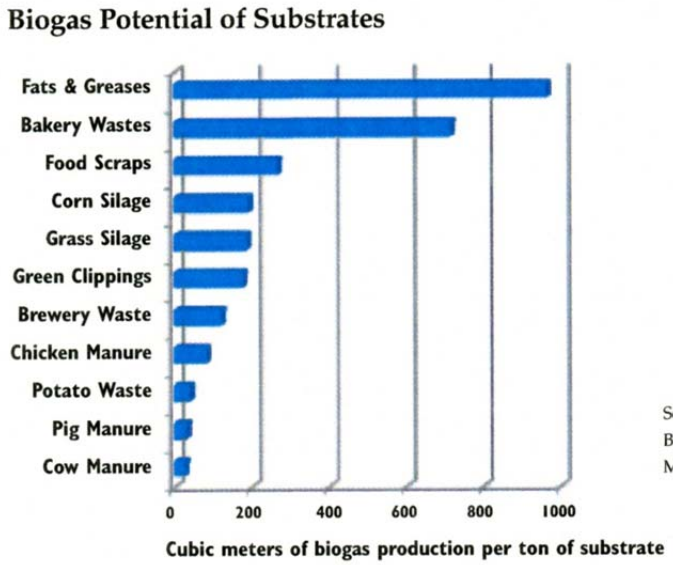


Figure 46. Relative biogas generation potential of different substrates expressed in cubic meters of biogas per ton of material (source: biogasenergy.com, 2007).

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LEGAL NOTICE

APPENDIX A

BIOMASS-DERIVED DISTRIBUTED GENERATION OF FERTILIZER

BIOMASS-DERIVED DISTRIBUTED GENERATION OF FERTILIZER

Executive Summary: The Energy & Environmental Research Center (EERC) identified an opportunity to leverage Xcel Energy RD3-68 project funds as cost share to access federal funds for a complementary project to assess converting low-Btu anaerobic digester biogas into ammonia. A small laboratory-scale processing plant was designed and constructed to test the viability of converting biogas from anaerobic digesters and landfill gas to anhydrous ammonia. The goal of the project was to determine if small distributed-scale ammonia production can be economically accomplished in a rural setting, with the agricultural producers being responsible for their own supply of ammonia.

The entire plant was operated in two separate 5-day campaigns. The first campaign utilized simulated biogas as the feedstock. The second campaign utilized a shifted gas, resembling a syngas produced by low-temperature gasification. Both campaigns resulted in the production of ammonia from the stated feedstock.

Data resulting from the design, construction, and operation of the ammonia production plant support the effort to design larger economically viable units that may actually be deployed in field operations. Currently, a 3.3-short-ton-per-day plant and a 20-short-ton-per-day plant have been requested by separate potential partners.

Technical Progress: A block flow diagram of the process is illustrated in Figure A-1. Key operating units that were designed, constructed, and operated were 1) steam methane reforming (SMR), 2) high-temperature shift, 3) hydrogen purification, 4) nitrogen separation from air, 5) ammonia synthesis, 6) ammonia capture, and 7) unreacted hydrogen and nitrogen recycle. Other units that were designed and constructed include 1) steam generation, and 2) low-temperature shift. The steam generation unit was operated but eventually removed from the production train as it was learned that direct injection of water into a hot SMR reactor was more reliable. The low-temperature shift unit was not operated, as conversion in the high-temperature shift unit was sufficient for project needs.

A key challenge during the project was reconciling performance claims of vendors against actual performance achieved in the laboratory. In one instance this required redesign of a key operating unit and, in another case, return of a piece of equipment for replacement with a nondefective model.

A computer control program, complete with supporting electronics and instrumentation, was developed and constructed. This provided for PC-based control of most of the processing plant as well as data logging of key numerical parameters, especially temperature and pressure.

Design of the unit required a total of more than 3 months. Construction required a total of more than 4 months. Operation of individual units required more than 1 month, and operation of the entire plant in concert required 2 weeks.

Operating units were commissioned on an individual basis utilizing parametric testing of key operating variables and optimizing unit performance based on chemical analysis of the products

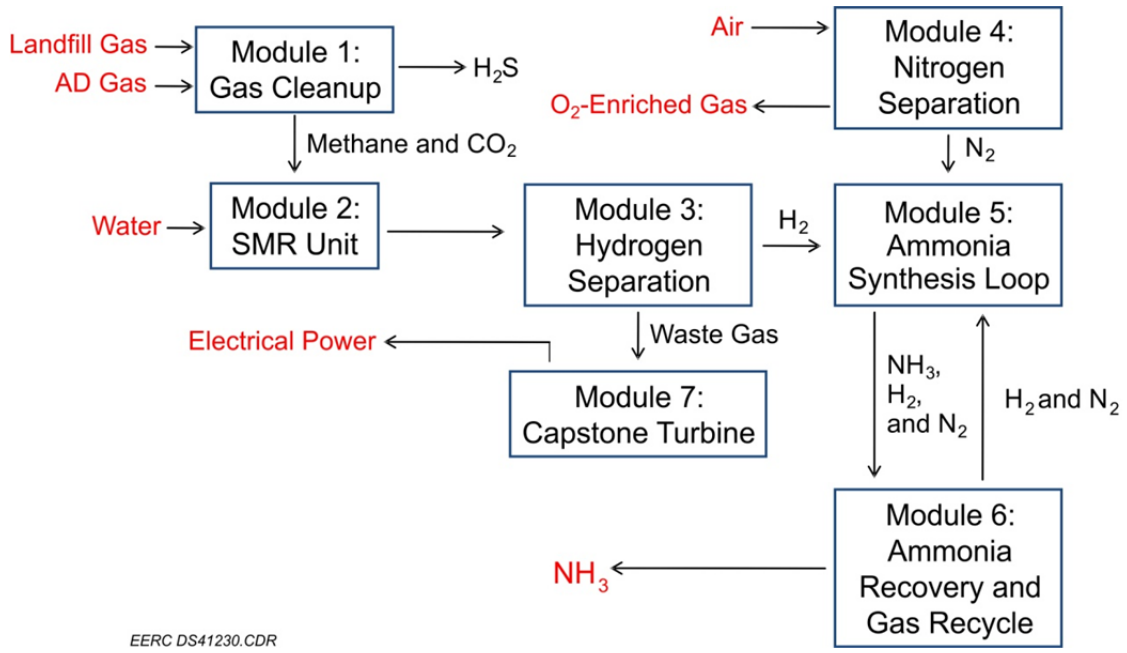

Figure A-1. Block flow diagram for process for conversion of anaerobic digester or landfill gas to ammonia.

formed. In several instances, performance of key units exceeded design specifications. In a few instances, minor adjusts (i.e., increasing catalyst load in a reactor) significantly improved unit performance and allowed the program to move forward.

A significant finding was that mixtures of methane and carbon dioxide, as commonly found in both biogas and landfill gas, can be directly reformed after removal of hydrogen sulfide and siloxanes, providing high conversion to hydrogen. That is, carbon dioxide removal from the methane is not required. Further, the results obtained were better than expected. Thermodynamic equilibrium calculations have been conducted to explain the results. While more study of this effect is required, it is presently thought that the water–gas shift reaction is playing a role in the high yields of hydrogen being attained.

Project Benefits: Ammonia is manufactured on very large scale around the world, with approximately 133 million metric tons of ammonia produced in 2009.[1] The primary feedstock for this production is natural gas, of which the main component is methane. The energy utilized to produce ammonia accounts for over 1.2% of all energy consumed in the world.[2] The range of energy consumption for production of 1 metric ton of ammonia is between 25 and 35 gigajoules (21.4 and 30.1 million Btu per short ton).[3] This translates to between 1.25 and 1.75 pounds of CO_2 emissions per pound of ammonia produced. It is the goal of the EERC to reduce the CO_2

[1] U.S. Geological Survey, 2010, Mineral commodities summaries, January 2010.
[2] International Fertilizer Industry Association, 2009, Energy efficiency and CO_2 emissions in ammonia production: 2008–2009 summary report, September 2009.
[3] Wood, S., and Cowie, A., 2004, A review of greenhouse gas emission factors for fertiliser production: Research and Development Division State Forests of New South Wales, Cooperative Research Centre for Greenhouse Accounting, June 2004.

footprint of ammonia production via substituting renewable resources for fossil methane. Another goal is to develop technology that will provide a price-stable means of ammonia production for utilization by agricultural producers.

Ammonia consumption in the United States amounted to 15,540 metric tons in 2009. Of this, 9350 metric tons was produced in the United States, and 6144 metric tons was imported. About 89% of this ammonia is used as fertilizer in the form of anhydrous ammonia, urea, ammonium nitrates, ammonium phosphates, and other nitrogen compounds.[3] Since foreign sources of natural gas are lower-priced, more foreign-produced ammonia has entered the United States over the past decade. As a result, the United States is becoming dependent upon foreign sources for cultivation of both our food and our fuel ethanol.

In addition to the needs stated above, ammonia is subject to cyclic price swings because of the cost of manufacture being closely tied to the cost of natural gas. This can result in a farmer paying $450 per ton in one growing season, and only a few growing seasons later having to pay more than $1200 per ton. For the farmer, this is uncontrolled variable cost that makes running a business challenging.

It is the purpose of this project to reduce fossil CO_2 emissions from the production of ammonia and to decouple ammonia production from the cyclic market price swings associated with natural gas.

Project Lessons Learned: The project has led to several interesting findings and several commercial possibilities. First, it has been determined that simulated biogas can be converted to ammonia in a chemical process. Second, the number of operating units required to perform this transformation is less than that associated with a traditional large-scale ammonia plant. Third, application of modern technologies allows for economically viable distributed-scale production via the pathways laid out in this project. Fourth, the economic tipping point for financial success is estimated to be at a production level above 700 pounds of ammonia per hour.

Commercial possibilities that have arisen as a result of this effort include utilization of the following feedstocks or energy sources: 1) biogas and/or landfill gas, 2) flare gas associated with petroleum extraction, 3) biomass conversion via gasification, and 4) wind-generated electricity for hydrogen production via water electrolysis. All these possibilities are currently being examined by senior EERC researchers in partnership with private-sector groups and individuals.

The finding that water-based reforming of mixtures of methane and carbon dioxide provide better-than-expected results has formed the basis of a patent application to be filed by the EERC.

Further work in the area of water-based reforming of methane and carbon dioxide mixtures is warranted. The EERC is presently seeking funding sources for this proposed effort.

Usefulness of Project Findings: Traditionally, the price of anhydrous ammonia is coupled with that of natural gas. A rough rule of thumb useful in calculating the real market value of anhydrous ammonia is to multiply the market price of natural gas by 35 (million Btu/ton), add $100 for operational expenses (per ton), and add another $50 to $100 (per ton) for transportation expenses. This formula, at today's market price for natural gas ($4.5/dekatherm) provides that

ammonia should be selling for $300 to $350 per ton. The current Gulf Coast price (August 1, 2011) is $560 per ton, FOB destination.

More recently, the price of ammonia has been tracking with that of corn (see Figure A-2[4]). This is a disturbing turn of events. In the past several years, the ammonia industry in North America has consolidated until there are only two major players in the industry. Agrium (Calgary, Alberta) has a strong market position in the northern plains, with numerous anhydrous ammonia production facilities supported by the abundance of natural gas in Alberta, and one production facility in Texas. The other major player remaining is CF Industries (Deerfield, Illinois), which possess one manufacturing plant in Iowa, one in Illinois, one in Florida, one in Mississippi, one in Louisiana, one in Texas, and two in Oklahoma.

It is anticipated that the technology developed at the EERC will be developed to provide for small distributed-scale production of anhydrous ammonia. Potential production costs have been estimated at $460 per ton. Implementation of this technology will provide a means to produce agricultural products in abundance with managed variable expenses. Therefore, not only will the Xcel Energy electrical rate payer benefit, but all people who consume agricultural produce grown with a nitrogen fertilizer will benefit.

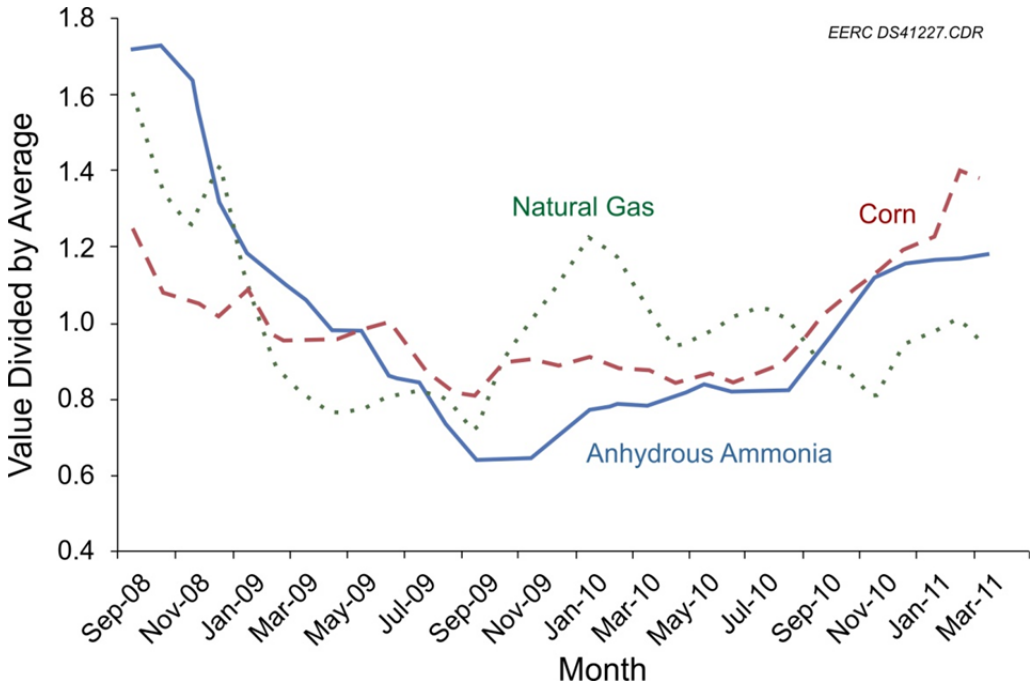

Figure A-2. Monthly anhydrous ammonia, corn, and natural gas prices, standardized by average for period September 2008 through March 2011.

[4] Figure obtained from The Crop Site (www.thecropsite.com/news/8608/anhydrous-ammonia-prices-likely-to-increase).