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FINAL PROJECT REPORT

RESEARCH TO DEVELOP BEST AVAILABLE CONTROL TECHNOLOGY FOR COMBINED HEAT AND POWER UNITS OPERATED ON DAIRY-DERIVED BIOGAS

Evaluating Emission Control Technology at the Fiscalini Farms Anaerobic Digester System

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PREPARED BY:

Primary Author(s):
Dr. Frank Mitloehner, Principal Investigator
Dr. Yongjing Zhao, Project Scientist
Yuee Pan, Staff Research Associate
Dr. Xing Jun Lin, Staff Research Associate
Dr. Sasha Hafner, Project Consultant
Curt Gooch, P.E., Project Consultant
Mianfeng Zhang, Graduate Researcher
Chris Weaver, Engine, Fuel, and Emissions Engineering, Inc.

University of California, Davis
One Shields Ave.
Davis, CA 95616-8504
Phone: 530-752-3936 | Fax: 530-752-0175
http://animalscience.ucdavis.edu/

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Prepared for:

California Energy Commission

Abolghasem Edalati
Contract Manager

Aleecia Gutierrez
Office Manager
Energy Efficiency Research Office

Laurie ten Hope
Deputy Director
ENERGY RESEARCH AND DEVELOPMENT DIVISION

Robert P. Oglesby
Executive Director

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PREFACE

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Research to Develop BACT for Combined Heat and Power Units Operated on Dairy Biogas is the final report for the Evaluating Emission Control Technology at the Fiscalini Farms Anaerobic Digester System project PIR-10-053 conducted by the University of California, Davis. The information from this project contributes to Energy Research and Development Environmentally Preferred Advanced Generation Program.

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ABSTRACT

Fiscalini Farms, a multi-generational dairy farm located in Modesto, California, underwent a two year, on-farm evaluation of their anaerobic digester power generation system that was conducted by the UC Davis Mitloehner lab under an agreement with the California Energy Commission.

Some sources contain more sulfur compounds then others and thus can result in increased biogas hydrogen sulfide (H_2S) concentrations that in turn increase the potential for increased exhaust gas oxides of sulfur (SOx) emissions. Due to the biogas hydrogen sulfide (H_2S) concentrations exceeding the San Joaquin Valley Air Pollution Control District (SJVAPCD) threshold limit of 50 ppm, the farm would normally have been required to implement a best available control technology (BACT) but was operating under a 'Variance' at the time of monitoring. Monitoring showed that H_2S turned out to be the only compliance issue because exhaust oxides of nitrogen (NOx) gas was found to be at acceptable levels from a regulatory perspective. A due diligence market investigation showed that an investment in a permanently installed H_2S reduction system was not an option financially, so a chemical mitigation option was implemented because it offered less initial financial risk to the farm and promised to work. Initial measurements showed that the chemical mitigation did not have a measurable effect in reducing biogas H_2S at first, but recent measurements by both the UC Davis research team and the regulatory agency in charge showed H_2S readings to be in the regulatory compliance zone.

In 12 of 14 sampling dates in 2014, oxides of sulfur (SOx) concentration measurements were zero and only two days showed above zero emissions. With H_2S present in the biogas but SOx emissions near zero overall, a conundrum is presented.

The study found that the former H_2S readings in the biogas were not well correlated with exhaust SOx, making H_2S a poor predictor. Furthermore, the team concluded that the present management of the anaerobic digester power generation is sufficient to keep all criteria pollutants as well as their precursors at allowable levels, making implementation of additional BACT unnecessary.

Keywords: anaerobic digestion, anaerobic co-digestion, CHP emissions, hydrogen sulfide, dairy regulatory compliance, emission control technologies, Guascor

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EXECUTIVE SUMMARY

Introduction

California ranks first in the nation in dairy production and also in dairy manure, sewage sludge, municipal solid waste, and food-processing waste generation. These organic by-products can be processed using anaerobic digestion technology (a naturally occurring process that takes place in an oxygen-free environment) to produce biogas, a gas that has significant methane content. The undeveloped biogas generation capacity at California landfills, dairies, wastewater treatment plants, and food processing facilities has been estimated to be about 184 million cubic feet of methane production, representing about 600 megawatts. Utilizing biogas from yet-to-be-developed anaerobic digester systems utilizing municipal solid waste, sewage sludge, dairy manure, and food processing wastes for renewable energy production will help California meet state Renewable Portfolio Standard goals and greenhouse gas emission reduction targets.

One significant ongoing barrier in development of biogas systems for dairies in California is in meeting California Air Resources Board (ARB) and regional emission standards for biogas-fueled engines. At this time, there are no biogas-fueled engine manufacturers or post-combustion emission control providers that can provide guarantees for emission controls that meet ARB 2007 standards for nitrogen oxides (NOx). However, the present project showed that use of at least one company's post-combustion emission control unit, which was recently introduced into the marketplace, resulted in emission rates for two criteria pollutants that comply with the ARB thresholds. But, unfortunately, the dairy-derived biogas combined heat and power (CHP) projects have largely ceased in California due to exhaust gas emission restrictions.

Addressing the State's regulatory emission standards requires ongoing technology development and associated testing/verification, operating experience, and economical analyses to establish viable BACTs. If new control options are identified, the market for dairy-derived biogas-fueled engines/CHP units will grow in California. Without this growth, no private commercial engine or emission control technology provider will sponsor major changes to their current engine and emission control technology design, which do not currently meet regulatory standards in California but is acceptable in most other states.

It is important to recognize that a CHP system operated on natural gas (virtually 100 percent methane) does not generate the same exhaust emissions profile as a CHP system operated on dairy-derived biogas (60 percent average methane content along with hydrogen sulfide (H_2S) and other gases). However, the emission requirements for dairy-derived biogas operated systems closely follow those of natural gas engines without regard to the more complex emission profiles of dairy-derived biogas. This creates a greater challenge for the dairy-derived biogas driven systems to meet regulatory compliance. Furthermore, with very limited experience and data to establish technically and scientifically sound emission standards for the dairy-derived biogas fueled engines, the regulators are left with enforcing standards on dairy-derived biogas systems developed from non-dairy-derived biogas applications.

Even if the State's air emissions standards are met, another important barrier to greater adoption of farm-based digesters in California, and the United States as a whole, is the economic benefit to the farm for these systems. Processing cow manure alone, while providing many environmental benefits, does not normally produce sufficient economic return on investment. Therefore, an important focus of this project was to present a business model that can offer increased electrical energy generation leading to increased revenue through the co-digestion of cheese waste from an on-site cheese production facility alongside manure and off-site generated organic materials as well as from other revenue sources for the system.

Because co-digestion of manure with other on- and off-farm sourced waste, or feedstock, sources impacts biogas volume and composition, it is also a factor that needs to be evaluated when determining BACT options. Some sources contain more sulfur compounds then others and thus can result in increased biogas hydrogen sulfide (H_2S) concentrations that in turn increase the potential for increased exhaust gas oxides of sulfur (SOx) emissions. Another factor in determining BACT options is the consistency of the availability and quality of off-farm sourced feedstocks. In most cases, this varies both by source and even over the course of time within a source, impacting the biological community in an operating digester and influencing the quantity of H_2S produced.

Utilizing alternative feedstocks in a dairy anaerobic digestion power generation system (ADPG) will benefit the environment through improved management of waste streams from food service companies as well as improvement of air and water quality. It is also important to demonstrate the viability of the system to the dairy operation through the recovery and/or sale of electricity, heat, environmental attribute credits and tipping fees. All of these revenue resources combined become very important when determining the economic viability of the project and promoting further commercialization of the technology.

The economic viability of this type of system is a critical component to the decision making of installing an anaerobic digestion power generation system on a dairy, with the additional potential revenue stream playing an important role in offsetting the extremely volatile milk industry economics.

Background

The technologies selected for the ADPG system project at the Fiscalini Farms included a complete mix mesophilic anaerobic digestion system designed and built by Biogas Energy, Inc. and a 710 kWh Guascor CHP skid-mounted unit by Martin Machinery, LLC and Gen-Tech, LLC. The results of a technical analysis performed in 2007 by both the Provost and Pritchard Engineering Group, Inc. and the USDA Natural Resources Conservation Service California State Engineer showed that the proposed AD and CHP technologies had technical merit.

This ADPG project was one of the first permitted by the Region 5 Water Quality Control Board to process (co-digest) more than one feedstock. The ability to permit a dairy digestion system utilizing more than one feedstock is critical to the economic viability and commercialization of this system.

The ADPG system consisted of two above-grade cast-in-place concrete tanks, each with a treatment volume of 850,000 gallons, for anaerobic digestion and an internal combustion engine-generator set designed to operate on dairy-derived biogas and to generate electricity and heat. The electricity produced was used on-farm and by the farm's cheese plant with the surplus being sold to the local utility.

When the farm evaluated the various biogas utilization options and associated digester technologies, the technologies they selected were a highly suitable configuration for their dairy operation. The various alternative uses of the biogas investigated included: fuel source for diesel engines (re-designed and re-built to operate on biogas) and microturbines and also for pipeline injection and fuel cells, both of which would have required additional gas clean-up measures. However, for each digester technology associated with these uses, Fiscalini Farms determined there were too many unknowns or uncertainties on top of the extraordinary implementation costs. Furthermore, in a commercial dairy setting, each of these technologies:

- had not operated as expected and/or failed,
- were the first projects of their type in a commercial dairy setting,
- were still in the experimental phase, or
- have historically experienced excessive engine break downs due to the re-configured old diesel engines not initially designed for biogas.

After extensive research of all of these technologies, it was clear that none had a proven track record in meeting the California air and water regulations. Many investigating these technologies have determined the following:

- the re-designed and re-built diesel engines will not meet the new air emission quality standards passed in May 2007 because of the SO_x, NO_x, particulate matter and CO emissions,
- the older diesel engines are getting harder to find and retrofit with the appropriate technology to bring them into the new air quality standards,
- the microturbine engines have problems with the higher H_2S levels in biogas, and their long-term operational success has not been demonstrated,
- the fuel cell technology has yet to be proven using exclusively dairy-derived biogas and the cost to install and operate is prohibitive for a dairy operation to manage,
- the biogas-to-pipeline gas option had not been proven to be a viable business model in the United States.

The anaerobic digestion technology used in this project was also new to California; the above-grade tank design was the first of its kind used on a California dairy. During the past 35 years, the typical anaerobic digester designs on California dairies have either been a below-grade covered lagoon style system or a below-grade "plug flow" design. The existing covered lagoon style AD technology has had trouble with key metrics: it has not consistently met California air

and water environmental regulations (possibly in part due to the inconsistent, naturally changing temperature within the lagoon affecting the overall biogas composition), it does not maintain a uniform production of gas year-round, and it requires a larger overall project footprint that may take valuable land out of production. Although there are 10 of these systems currently operating on California dairies (AgSTAR, 2015), developing a system with improved management of the waste material, higher efficiency and effectiveness in biogas production, and improved digestion of the organic matter will enable a greater economic return in a shorter period of time.

This system has been successfully demonstrated in Europe and in other states, but has not been tested in California in an agricultural environment—meeting existing California environmental regulations, primarily air and water regulations, is crucial to ensure commercialization.

Project Purpose

The purpose of this project was to identify and evaluate existing, readily available technologies as candidate BACTs for dairy-derived biogas-fueled CHP systems; collect system performance data for future use to advance the science, technology, and market penetration in California of distributed energy generation systems; and help the State achieve its renewable portfolio standard goal and greenhouse gas emission target.

Project Process

At the onset of the project at Fiscalini Farms Dairy in January 2013, the performance of producing biogas by the anaerobic digester and associated power production of the CHP was dismal. The UC Davis team identified: (1) insufficient digester organic loading rates with high energy feedstocks, (2) high levels of inorganic matter loading rates which make no biogas and adversely affects digester performance over time, and (3) a lack of proper mixing inside the digesters as the main reasons for poor gas production. Indeed, all three issues turned out to be main reasons for poor digester performance.

Therefore, the UC Davis team entered into discussions with the San Joaquin Valley Air Pollution Control District (SJVAPCD), who required Best Available Control Technology (BACT) for Fiscalini Farms due to H_2S concentrations of digester gas exceeding the SJVAPCD threshold limit. The actual concern of the SJVAPCD is SOx but instead of measuring it directly in the exhaust, the agency uses H_2S in the biogas as a predictor of SOx. Indeed, this exceeding of the threshold H_2S limit turned out to be the only compliance issue because other gases such as NOx were found to be at acceptable levels from a regulatory perspective and remained that way over the course of the project.

As a result of the initial monitoring findings, the team focused efforts on identifying valid options for H_2S removal and technology vendors for the options selected. Four companies were identified and contacted; at the research team's request, they provided written proposals based on information provided to them regarding the Fiscalini Farms anaerobic digester system and associated biogas characteristics. One of the companies, American Biogas Conditioning, was in the business of providing stand-alone biological oxidation systems, while the other three companies dealt in stand-alone chemical/physical systems utilizing iron oxide as the active

media. An advantage to all systems is they can be retrofitted into an existing biogas system. Of the three chemical/physical vendors contacted, two turned out to only be providers of iron oxide, and the other, MV Technologies, not only provided the iron oxide but also performed system design and installation.

After careful review of the four proposals, MV Technologies was considered the most promising system. The company had experience in developing systems for H_2S removal from biogas in similar applications. Their iron oxide-based system included a biological component that, according to the company, extends the media life and results in a lower operating cost than alternatives. However, MV Technologies was unable to provide any performance data for their system. Very limited data from a similar installation suggests that the MV Technologies system may have been able to provide a H_2S concentration below 50 ppm. MV Technologies did provide a performance guarantee for their system, but the guarantee was based on cumulative H_2S removal and not on processed biogas H_2S concentrations.

Ultimately, Fiscalini Farms decided to not move forward with any four proposals, due to the uncertainties in the performances of various vendors and lack of track record under comparable applications. These uncertainties posed a significant financial risk that the farm was unable to take. Therefore, focus by the project team was turned to quantifying and evaluating the effects of adding an additive, ferric chloride (FeCl), to the feedstock stream. The effects of the addition of FeCl directly into the digesters were analyzed on the resulting biogas H_2S concentrations and related engine-generator set exhaust gas emissions.

Ferric chloride was added to the each of the two digesters over two application periods during the course of this study with the overall goal to further reduce biogas H_2S concentrations over and above what was being achieved in the biogas head space of each digester vessel where an *in situ* biological reduction process was already taking place. Application period 1 was from April 15 to May 20, 2014 while application period 2 was from September 22 to October 1, 2014. During each application period, 15 lbs/day was added to each digester, with the initial concentration of 200 ppm FeCl being reduced to 100 ppm. The unit cost of the FeCl was reported to be $0.20 FeCl per pound delivered based on the quantities (275 gallon/tote) purchased.

Results

Total H_2S mass flow in biogas was related to the H_2S concentration and biogas flow rate. Flow of H_2S was found to be highly variable, but was generally below 5 kg S/d (11 lb_m S/d). As with H_2S concentration, lack of data limited the certainty of this estimate.

Overall, the measured biogas H_2S concentration during the period FeCl was added over the course of the project was 255 ppm (n = 11 days, range = 25 to 676 ppm) and was 181 ppm (n = 20 days, range = 82 to 490 ppm) during the period when it was not added. This suggests that FeCl had no meaningful reduction of biogas H2S concentration, possibly due to low application rates. However, toward the end of the project, H_2S in biogas has been reduced to less than the required 50ppm.

From an exhaust gas regulated emissions standpoint, no SOx emissions were found on 12 of the 14 sampling days. However, because there was no measured exhaust SOx on 12 days, yet at the

same time H_2S was measured in the biogas fueling the engine-generator set, the exhaust has to contain sulfur compounds.

Further investigation into this resulted in some interesting information that was provided by Weaver (2015). He indicated that the combination of the Selective Catalytic Reduction (SCR) system and exhaust heat-recovery likely provided an unanticipated benefit for the control of SOx emissions. At intermediate temperatures, ammonia slip from the SCR system may have combined with SO_2 to form solid ammonium bisulphate. The exhaust heat recovery system could have cooled the exhaust enough to remove both ammonia and SO_2 from the exhaust stream and depositing them in the heat-exchanger tubes.

A second explanation relates to the actual SOx measurement instrumentation. The instrument type that had been used at Fiscalini Farms by both the San Joaquin Valley Air Pollution Control District (SJVAPCD) and the UC Davis team, a Testo 350XL, yielded zero exhaust emissions on the majority of days in 2014. A co-location sampling event with two Testo analyzers (one owned and operated by the SJVAPCD staff and one by the UC Davis team), both yielded zero emissions in exhaust air. This poses the question that this is a measurement error in this instrument type that causes zero readings despite SOx being present. One such reason could be that within the Testo, the hot engine exhaust air is being cooled down, and this process generates liquid condensate, which the team's research has found to collect sulfur. It is possible, and subject to future research, that indeed some sulfur gets trapped in the instrument's condensate liquid and that some SOx never reaches the actual gas sensors within the monitor. How much this process is involved in the resulting readings of SOx is unknown but considering that the Testo XL is a standard monitor used across air districts throughout the US, this is an important issue to address to avoid costly regulation without affecting pollution mitigation.

Both explanations, sulfur deposits in the heat exchange unit and the potential of sulfur sampling errors inside the Testo units, have not been described in the scientific literature and will be subject of future research. This will be essential to understanding whether the Fiscalini Farms AD and CHP units are already in compliance with current rules to minimize NOx and SOx or if additional BACT is indeed warranted.

Benefits to California

Utilizing biogas from anaerobic digester systems utilizing MSW, sewage sludge, dairy manure, and food processing wastes for renewable energy production will help California meet state Renewables Portfolio Standard goals and greenhouse gas emission reduction targets. The results of the present project show that both SOx and NOx emissions from the Fiscalini Farms dairy were reduced or even eliminated. The system used a commercially available exhaust gas scrubber, and it appears that the combination of the gas scrubber with the cooling effect of the exhaust gases by the exhaust gas heat recovery system contributed to the results. If such results can be verified and duplicated, the roadblock issue of criteria pollutant emissions from biogas-fueled engines in California may be resolved. If so, the impact in California can be significant in several ways:

- A significant barrier for market development of distributed energy generation systems will be removed, helping the State achieve its Renewables Portfolio Standard goal and greenhouse gas emission target.
- Dairy farms can expand and diversify their business by securing economic value for the electricity produced and tipping fees received from off-site generators of organic wastes.
- By routing biomass into digesters versus landfills, California residents can benefit by avoiding the fugitive greenhouse gas emissions associated from landfilling organic materials.

CHAPTER 1: Introduction

1.1 Farm Overview

The Fiscalini family traces its roots back to 1705 in Switzerland, and in the 1890's, Mateo Fiscalini migrated to the United States from his home country and started producing and selling milk in California. The family relocated to Modesto, California in the 1920's, and at the time of this report, a descendent, John Fiscalini, milked 1,500 Holstein dairy cows and raised 1,500 replacement animals (heifers) on his 530-acre farm. Crops grown to feed the dairy cattle include silage corn, wheat and Sudan grass. These silage sources are mixed with other dairy cow feedstocks (e.g., ground dried corn, soybean meal, cotton seed, almond hauls) on a daily basis and the result, a total mix ration (TMR), is fed to the cows each day. The exact amount of each TMR component is determined by a dairy cow nutritionist based on several factors (e.g. target milk production, stage of milk production, time of the year). A Google Earth image of the Fiscalini farmstead is shown in Figure 1.

Figure 1: Google Earth image of the Fiscalini farmstead

Source: Google earth

Producing high quality milk has always been a goal of Fiscalini Farms. With the construction of a cheese plant in 2000, producing quality milk has paid big dividends by contributing to the quality of their award winning cheeses produced on the farm.

1.1.1 Cow Barn Configuration/Manure Collection

The management style of Fiscalini Farms was similar to most California dairies, in that the cows are housed in freestall barns that are flushed with recycled water multiple times a day to remove the manure from the barn floors. Research has shown that the average Holstein milk cow in the United States produces 150 pounds of manure per day composed of 130 pounds of moisture and 20 pounds of solids (ASABE, 2006).

An immense amount of water is needed to flush the barn floors (in excess of 140,000 gallons per day) resulting in a very low manure solids concentration in the flushwater discharge stream. The majority of the flush water is re-used and is not fresh water. The flush lanes were approximately 900 feet long and were normally flushed 6 times per day for 2-3 minutes at a flow rate of approximately 1,000 gallons per minute. There were 4 barns with 2 lanes per barn and each barn housed approximately 450 dairy cows. Each flush lane discharge was collected into a common concrete conduit and flowed into an inlet structure located at the digester.

The inlet structure for the flushed manure was divided into 4 separate concrete basins. Basin number one was used to settle the heavy, primarily non-organic, particulates from the flow. This included sand, dirt, rocks, and other materials unsuitable for the anaerobic digestion system. From the initial inlet structure the manure slurry flowed into the East pumping chamber where the slurry was pumped across a slope screen separator (a device which separates the large solids from the slurry mixture) where the discharge gravity flowed into the settlement pit. The settlement pit basin was originally designed and built to feed the digester from the conical bottom.

The use of the original flow scheme allowed a very high percentage of inorganic solids to pass through the slope screen into the conical bottom basin. These inorganic solids, primarily sand, were then pumped directly into the digester tanks. Due to the density of the inorganic materials, it settled out in the digestion vessels, causing serious pre-mature wear issues to the mixers and pumps and ultimately led to the multiple failures of the mix system in digester tank 2. Digester tank 2 was emptied and cleaned three times, the last time being in June 2013, when digester tank 2 was pumped out and the inorganic buildup was removed with a skid-steer loader (Figures 9 and 10). The mixers were repaired and re-installed and tank 2 was returned to service the end of July 2013, after being out of commission for 7 weeks. This buildup of inorganic materials was similar to the other two times the tank had to be emptied and cleaned.

1.2 Anaerobic Digestion System

Fiscalini Farms began investigating the possibility of building an anaerobic digester system in 2006. The idea of building a digester came from an article in the local newspaper, the Modesto Bee, whereby the San Joaquin Valley Air Pollution Control District (SJVAPCD) Board suggested that dairy farms in California were a significant source of greenhouse gas emissions. While the

data used by the Board was subsequently proven to be inaccurate, there remains a great deal of public concern about methane emissions from dairy farms.

Realizing the overall benefits of anaerobic digestion of manure and in an effort to be proactive in realizing these benefits, Fiscalini Farms initially focused efforts to identify the most appropriate technology and associated vendors to implement it in early 2007. Biogas Energy Systems, LLC was chosen to build the digesters and Martin Machinery was selected to supply the engine-generator set. Cal Coast Manufacturing, a local builder, worked in conjunction with both companies to construct anaerobic digester system. The system became fully operational on June 1, 2009.

The anaerobic digester system included two circular above-grade insulated tanks operating in parallel to each other. Each tank was 86 feet in diameter and 26 feet tall and held approximately 860,000 gallons. The tanks had 14-inch thick reinforced, cast-in-place concrete walls and an 18-inch thick concrete floors that were designed and constructed according to California seismic regulations, using 500 cubic yards of concrete and 50 tons of reinforcing steel per tank.

Both tanks had one-inch-diameter heating tubes spaced every six inches apart, wrapped around the perimeter of the entire tank height; heating coils were also placed within the concrete floors. In both locations, the heating pipes were just below the inner surface of the concrete to maximize the heat transferred from the pipes to the digester contents, keeping it at the target temperature of 100 F. Below each tank, and also around each tank's outer perimeter was two inches of closed foam insulation used to minimize the heat lost from the tanks. Corrugated painted steel panels were used for the exterior architectural cladding and to hold the insulation in place.

Inside each tank there were four Flygt submersible mixers used to blend the contents to a homogenous state. These mixers were suspended on a cable system allowing them to be raised and lowered in the digester column. The mixers were also configured with a manual rack-and-pinion system allowing them to be rotated within the digester. This configuration allowed changes to be made to the mix systems while the digester was in operation.

Flow into the digester (influent) includes flushwater from the dairy cow and heifer barns, cheese whey from the farm's cheese plant, and in some years Sudan grass silage.

The biogas was contained within the head space of the digester vessels using a gas-tight dual membrane (60 mm polyethylene) containment system. The space between the two membranes was inflated using ¼ horsepower air blowers to keep the membrane system taught. The membrane system was stretchable so that it could expand to hold biogas not used immediately for up to 18 hours if needed. A wooden truss system provides support for the membrane system for each tank. The digester vessels were equipped with several safety devices designed to prevent over- pressurization of the tank, thus minimizing the risk of catastrophic failure.

A small amount of ambient air (normally 3 to 4 percent on a volume basis) was blown into the headspace of the digesters to promote the growth of low oxygen concentration-demanding (facultative) microorganisms; these microorganisms naturally convert some of the H_2S

generated from the digestion process into insoluble sulfur compounds. These compounds slough off and were removed via the digester effluent withdrawal. Using the air injection system typically decreases the H_2S concentration from approximately 2,000 - 4,000 parts per million (ppm) to under 500 ppm.

Biogas was piped from the gas headspace of each vessel using high-density polyethylene piping and a blower unit to the biogas-fueled engine-generator set. Prior to utilization, the biogas was cooled to approximately 45 F to condense some of the biogas moisture vapor and to increase the energy density by reducing the overall volume of the biogas, thus increasing the energy density on a volume basis.

Biogas was used as the fuel source for a Spanish-built Guascar 500 series engine (V-12 1,057 horsepower) that was designed to solely burn biogas (see Figure 2). The engine was connected to a 710 kW generator. The combined heat and power (CHP) unit produced both electricity and hot water. The electricity generated was first used by Fiscalini Farms dairy farm and Fiscalini Cheese Company's cheese making facility with surplus sold to the local utility — Modesto Irrigation District. The CHP unit's 710 kW of electrical generation capacity was enough to meet the farm's electrical demand and also to power 100-200 homes in the nearby community. In addition to the electricity, combustion heat produced by the engine was harvested using two heat exchangers; this heat provided sufficient hot water to: (1) keep both the digester tanks operating at 100 F; (2) meet the hot water demand for the sanitation needs of the dairy farm and cheese plant; and (3) meet the hot water demand for the cheese plant for the milk pasteurization process and for process heat for the cheese vats.

Figure 2: Guascar CHP system fueled by biogas produced by two anaerobic digesters at Fiscalini Farms

Source: UC Davis

The engine was equipped with a selective catalytic reduction (SCR) unit. This unit's function was to remove the majority of the nitrogen oxide (NOx) and carbon monoxide (CO) emissions from the exhaust.

A portion of the heat generated from the combustion process was captured in a heat exchanger system; heating water was used as a means of moving the heat to the digester tanks and other parts of the dairy. This hot water was circulated through the piping system described above to maintain the digester at 100 F. The Gauscor gen-set and the associated heat recovery systems were designed and installed by Martin Machinery. All of the electricity generated by the CHP was sold to the Modesto Irrigation District, the local electrical utility, under a 15-year power purchase agreement.

Digestate (effluent) from both digesters was piped to a set of screw press solid-liquid separators. Separated solids were used to bed the freestalls and separated liquids were stored and recycled to the land base as organic fertilizer for the forage crops grown.

CHAPTER 2:
Biogas Composition, Clean-Up, and Exhaust Gas Scrubbing

2.1 Biogas Basics

Biogas is similar to natural gas which is nearly 100 percent methane (CH_4); however, biogas also contains a significant portion of carbon dioxide (CO_2) and small quantities of water vapor (WV), hydrogen sulfide (H_2S) and trace gases. Biogas is formed when the microbes within a digester vessel decompose organic material, transforming it into CH_4 and CO_2. Methane is the source of the energy that can be harvested from biogas.

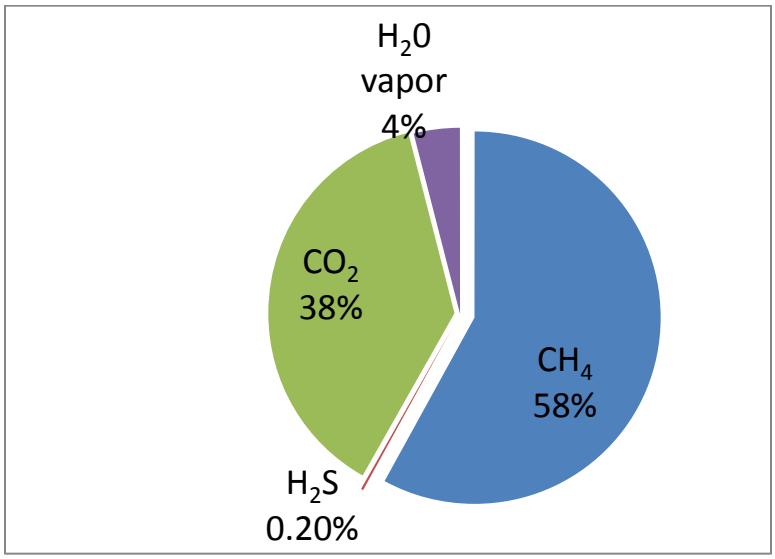
Biogas is saturated with water vapor when it leaves the digester. Hydrogen sulfide, in conjunction with the water vapor, is corrosive to burner units and heat exchangers in boilers, furnaces and water heaters and accelerates the development of acidic conditions in engine oil.

2.2 Biogas Composition

Dairy manure derived biogas is composed of the following gases at the approximate ranges shown (Figure 3):

- Methane (CH_4); 55 to 68 percent
- Carbon Dioxide (CO_2); 32 to 45 percent
- Hydrogen Sulfide (H_2S); 1,500 –5,000 ppm
- Ammonia (NH_3); 0 –300 ppm
- Water Vapor (WV) in saturated gas; 3-4 percent

Figure 3: Primary gases at approximate concentrations constituting biogas at 76F.

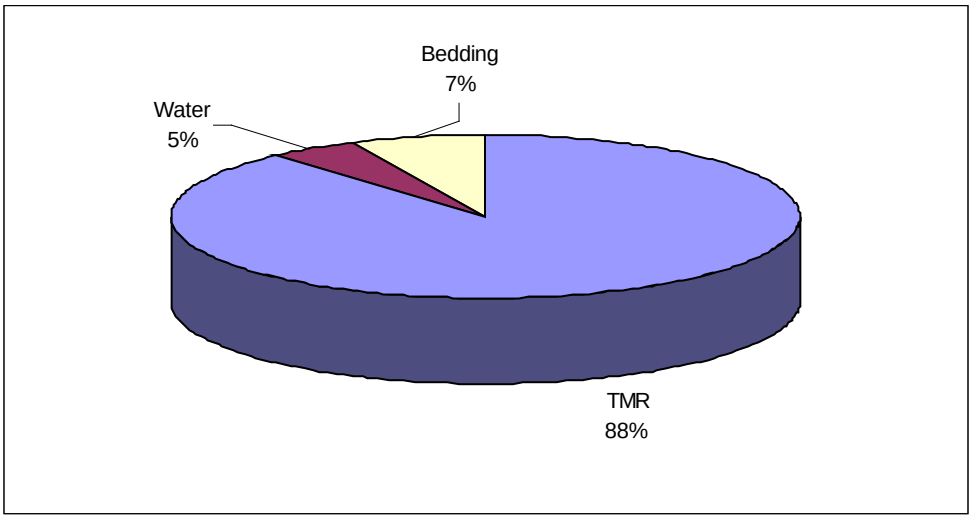


Source: Ludington and Weeks, 2008

Gas quality depends on energy content, H_2S content, water vapor content, and presence of contaminants from the gas handling equipment. While not necessarily considered a gas quality issue, contamination from digester foaming is also a related condition.

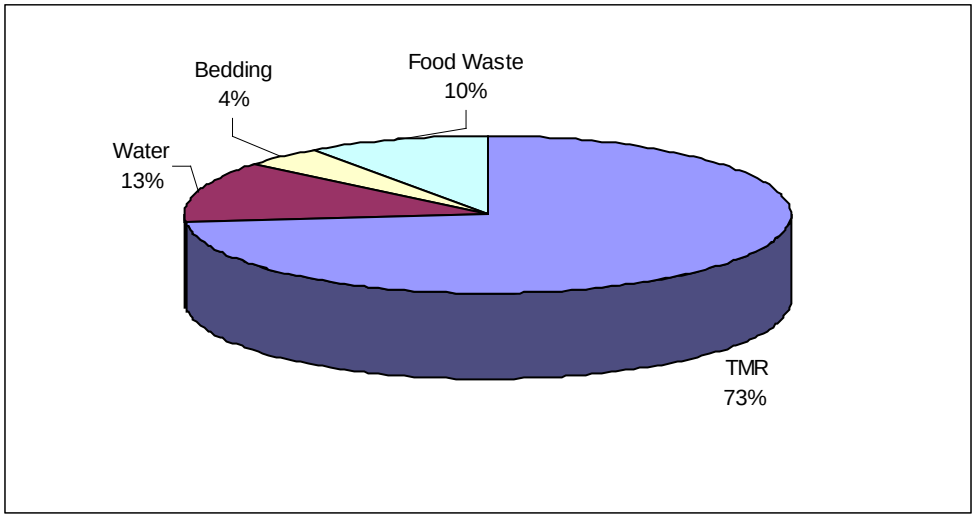
The percentage of H_2S found in biogas can be as high as 0.5 percent with influencing factors being levels of sulfur in the cattle feed ration and drinking water and sulfur in non-manure components of the digester influent stream. To better understand and quantify the sources of sulfur in digester influent, a field study was performed by Ludington and Weeks (2008) to determine where the sulfur in the H_2S component of biogas was originating. Eight New York State dairy farms with operating digesters were extensively monitored. The two graphs shown in Figures 4 and 5 are the final overall aggregated study results of the source of sulfur in the case of non-co-digesting systems as well as in co-digesting systems (Ludington and Weeks, 2008).

Figure 4: Sources of sulfur in digester influent for farms not co-digesting.



Source: Ludington and Weeks, 2008

Figure 5: Sources of sulfur influent for farms co-digesting imported substrates.



Source: Ludington and Weeks, 2008

Potential but not likely contaminants in dairy manure-derived biogas include the following, typically found in other sources of biogas (i.e. landfill-generated biogas):

- Siloxanes
- CFCs
- Oxygen
- Nitrogen

Co-digestion operations have a possibility of encountering one or several of these contaminants.

2.2.1 Biogas Clean-up

Biogas clean-up can be performed at various levels, from simply removing moisture to more advanced clean-up strategies to produce biomethane (also known as renewable natural gas or RNG) for injection to a natural gas pipeline or for use as a vehicle fuel. The following list distinguishes the different aspects of varying levels of biogas clean-up:

- Low-level biogas clean-up involves removal of some moisture for transport in a local pipeline.
- Mid-level biogas clean-up involves removal of H_2S and sometimes additional moisture as well, in order to use biogas in on-site combustion.
- Advanced-level biogas clean-up can involve the removal of:
    - hydrogen sulfide
    - water vapor
    - carbon dioxide
    - ammonia

To produce biomethane, the concentration of H_2S, moisture and carbon dioxide in biogas must be significantly reduced. Biomethane can be compressed for long distance transport; however economic implications usually make this an unfavorable pursuit.

The following sub-sections outline several technologies that are utilized to remove or to significantly reduce specific contaminants from biogas. There are several places where technologies achieve reductions/removals of more than one of the contaminants mentioned, so it should be cautioned that the entire section should be read when assessing different technologies available.

2.2.2 Moisture Removal

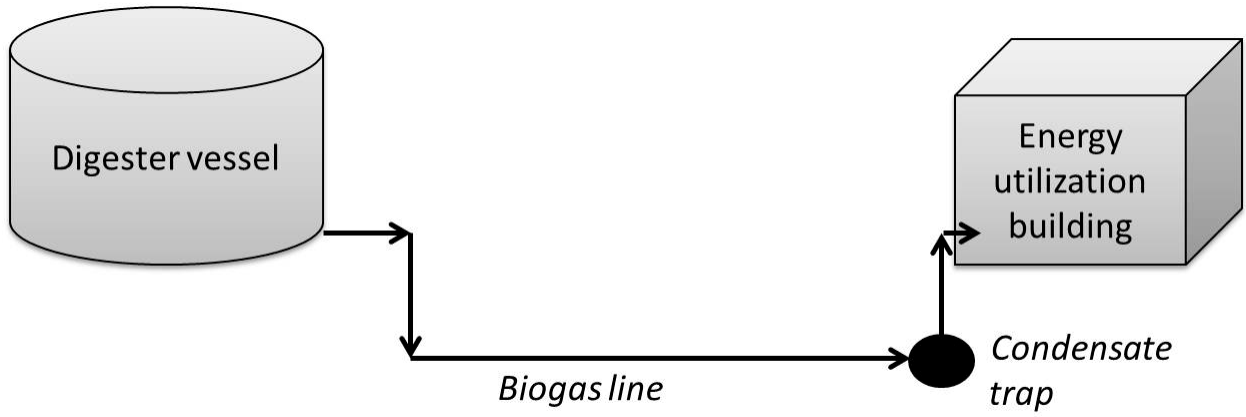
There are several strategies to remove moisture (i.e., water vapor) from biogas, which is desirable for multiple potential end-uses: passive moisture removal (condensate trap), refrigeration, use of adsorption agents, and pressure swing adsorption. These strategies are outlined below.

The most basic way to remove moisture from biogas is a passive strategy that uses the temperature differential of the biogas leaving the digester and the biogas being piped underground. A condensate trap at the end of the biogas pipe collects moisture that has condensed out due to the cooler temperatures below ground. This strategy is shown in Figure 6.

Another strategy used to remove moisture from biogas is refrigeration. Heat exchangers are used to cool biogas to the desired dew point before biogas is pressurized to promote additional drying. The condensate is removed from the system and disposed of as wastewater. Another strategy to remove moisture from biogas is through adsorption. Adsorption agents are used to

capture moisture in the biogas, and silica gel or aluminum oxide is used when biogas is destined to be used as a vehicle fuel. In this case, two vessels are used to provide continuous treatment opportunities.

Figure 6: Using a condensate trap to passively remove moisture from biogas.



Source: Cornell PRO-DAIRY Program

2.3 Hydrogen Sulfide Removal from Biogas: Physical/Chemical

2.3.1 Iron Sponge

An iron sponge system is an above-ground, usually cylindrical tank located between the digester and biogas utilization system. An example is shown in Figure 7. The tank contains wood bark impregnated with iron oxide (15 pounds of iron oxide per 1 bushel of wood). One bushel of wood bark occupies 1 cubic foot of space in the tank.

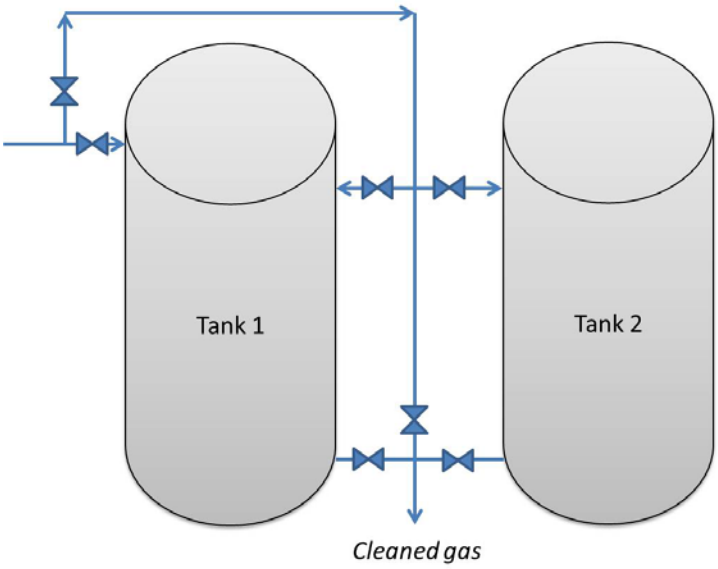
The tank should have a diameter to active height ratio of 1:1 to 1:15 in order to promote uniform exposure of the biogas to the bark media and to limit the pressure drop across the media, which is 2-3″ water column initially and 8-10″ after being utilized for treatment for some time. Biogas blowers are needed to force the biogas through the iron sponge and must be appropriately selected. Multiple tanks are used in most systems so one or more tanks are always available to process biogas. With multiple tanks, a piping system that is strategically laid out provides flexibility in biogas flow directions so the tank with the newest or most recently regenerated iron sponge is providing the final cleaning as shown in Figure 8.

Most iron sponge clean-up systems have an in-vessel spray system to ensure the wood chips are saturated with moisture. However, because dairy manure-derived biogas is saturated with moisture, and the vessel will be operating at a temperature less than the temperature of the biogas at exit from the digester, condensation will likely occur readily in the vessel resulting in times when the in-vessel spray system is not needed. The vessel should have a condensate drain at the bottom to drain off excessive moisture.

Figure 7: Iron sponge biogas clean-up system on a dairy farm AD system.

Source: Cornell PRO-DAIRY Program

Figure 8: H_2S scrubber system with multiple tanks, providing the opportunity to regenerate the media in one tank while continuing to process biogas in the other(s).



Source: Cornell PRO-DAIRY Program

The chemical reaction that occurs within an iron sponge system at ambient temperatures results in the physical bond of sulfur to iron oxide. Alkaline conditions, defined as having a pH greater than 7.5, must be present to support this reaction. For each pound of iron oxide (FE_2O_3) present

in the system, 0.56 pounds of sulfide can be removed from the biogas. Iron oxide can be regenerated by adding air (O_2), which prolongs the life by 3-4 times. Through this process, the sulfide is changed to elemental sulfur. When H_2S is no longer removed and/or when the wood bark has deteriorated, spent iron sponge material can be burned, land-filled or spread on agricultural land.

2.3.2 Activated Carbon

The chemical removal of H_2S from biogas can be achieved with activated carbon impregnated with either potassium iodine or sulfuric acid. Air is injected into biogas to promote carbon adsorption of hydrogen sulfide. Carbon is also regenerated with injected air. The sulfide is changed to elemental sulfur.

2.4 Hydrogen Sulfide Removal from Biogas: Microbial

2.4.1 Biological Fixation

Air is injected into biogas at a level of 2-4 percent, while a medium is provided for microbes (*Thiobacillus sp.*) to adhere to. The operative microbes grow on the surface(s) provided and reduce H_2S concentrations down to 60-200 ppm, at the same time reducing ammonia (NH_3) concentrations. This process can take place either in the digester headspace (i.e. *in-situ*) or in a separate vessel.

2.5 Hydrogen Sulfide Removal from Biogas: AD Influent Additives

2.5.1 Ferric Chloride Dosing

Diluted ferric chloride (FeCl) can be injected directly into a digester by an automated dosing unit, but is more likely to be added to the digester influent pit. It is good for treating high initial H_2S concentrations as the first step in a multi-stage removal process. Initial costs are low, but the operating cost can be considerable due to daily chemical use.

Ferric chloride is an iron salt which is applied for hydrogen sulfide control, phosphorus removal, sludge thickening, conditioning, as a dewatering agent, and for chemically enhanced clarification. Solutions of iron salts control H_2S and associated odors by precipitating it from aqueous solution. The ferric chloride precipitation reaction is shown in the following overall reaction:

$$2FeCl_3 + 3H_2S \leftrightarrow Fe_2S_{3(s)} + 6HCl$$

The reaction demonstrates that 1 mole of Fe^{+3} precipitates 1.5 moles of H_2S. The actual precipitation reactions will depend on what soluble form the sulfide is in, as hydrosulfide (HS^-) or sulfide (S^{-2}).

The recommended ferric salts dosage for H_2S applications vary somewhat depending on the control strategy chosen by the end user. For example, if the treatment objective is to control the liquid phase sulfide concentration, then the recommended ferric salt dosage is 110 - 125 percent of the stoichiometric dosage (based on the difference between the existing and target liquid-phase sulfide concentrations). Slight overdosing is recommended to insure achieving treatment objectives. If the treatment objective is to control the vapor phase H_2S concentration, then the

recommended ferric salt dosage is 125 percent of the difference between the existing liquid phase sulfide concentration and an assumed "target" liquid phase sulfide concentration that will generate the target vapor phase H_2S concentration. Note that since these systems are open, there is no true equilibrium between the vapor and liquid phases. Thus, an inexact relationship exists between the vapor and liquid H_2S concentrations, making this a somewhat trial-and-error approach. Other complicating factors include the presence of phosphorus, organics, and other compounds, which consume the available iron in the system.

The two most utilized ferric salts are ferric sulfate and ferric chloride, commonly sold and applied in a liquid form. Ferric chloride is sold in a higher strength. The advantage of ferric sulfate versus ferric chloride solutions is the compatibility of the iron salts with metals.

2.6 Engine-Generator Set Exhaust Gas Scrubbing

2.6.1 Overview

Lean-burn spark-ignition engines are reliable, efficient, and economical prime movers for electric generators, pumps, and other mechanical drive needs up to about 3 MW (4,000 horsepower). By using the waste heat from the engine, combined heat-and-power (CHP) systems can reach overall efficiencies much higher than the best central power plants – saving money and reducing greenhouse emissions. Even larger savings and emission reductions can be reached using renewable fuels such as biogas and gasified biomass.

Although they can lower greenhouse emissions, lean-burn engines have relatively high emissions of oxides of nitrogen (NOx), an important contributor to smog. Until recently, increasingly strict emission limits have largely stymied the spread of CHP and other distributed generation technologies in California and in other states with serious air pollution problems.

Selective catalytic reduction (SCR) is the most effective emission control technology for lean-burn engines (Weaver, 2015). Until recently, though, the only SCR technologies available were designed for large power plants. These systems were too big, too complicated, and too expensive to be practical for most engine installations. However, at least one company, Engine, Fuel, and Emissions Engineering, Inc. (EF&EE) has developed the application of compact, high cell-density SCR catalysts to non-road and stationary engine applications.

2.6.2 How SCR Works

SCR works by adding a small amount of a reductant chemical to the exhaust upstream from a catalytic converter. Commonly-used reductases are ammonia and urea (which breaks down to form ammonia in the hot exhaust). The catalyst in the converter selectively promotes the chemical reaction between the ammonia and NOx. This reaction converts both the ammonia and the NOx into harmless nitrogen gas and water vapor.

The amount of reductant needed for NOx control varies with the amount of NOx in the exhaust. Too little reductant means that some NOx escapes un-reacted, while too much means leftover ammonia in the exhaust (ammonia slip). Programmable controllers are used to vary the reductant injection rate to match the NOx emission rate from the engine.

2.6.3 Application in California

At least one company's SCR system has been accepted as BACT for stationary internal-combustion engines under California regulations. To be accepted, they have demonstrated emission levels below the BACT limit of 0.15g /BHP-hr (11 ppmvd) of NOx in engines running on natural gas, biogas, and LPG.

CHAPTER 3:
Digester Performance at Fiscalini Farms in Early 2013

3.1 Summary

The Fiscalini Farms Dairy anaerobic digestion system was designed to treat manure wastewater from 1,500 cows and was expected to produce a maximum of 710 kilowatts of electricity. At the onset of the present project at Fiscalini Farms Dairy in 2013, the system had suffered from an accumulation of sediment in both digesters and resulting low electricity generation. These problems appeared to have been caused by:

- the low solids content of the manure wastewater, resulting in a low viscosity that prevented suspension of solids,
- insufficient mixing, which had been exacerbated by mixing nozzles plugged by cow pedometers and other debris, and/or
- insufficient organic matter loading.

3.2 Digester Loading of Organic and Inorganic Matter

In early 2013, the organic matter loading from manure was about 2,000 pounds per day, and it contributed to only about 20 kW of electrical power[1]. Total electricity production at that time was around 100 to 150 kW. Food waste volume was between 150,000 and 250,000 gallons per month (average of 5,000 to 8,000 gallons per day), but the composition was variable. With a total reacting volume of about 850,000 gallons, the hydraulic retention time for digester 1 was between 25 and 30 days.

The two primary problems with the operation of the system in early 2013 and before were low electricity production and solids accumulation which interfered with mixing and reduced reactor volume and retention time. In terms of operating the digesters, inorganic (non-digestable) solids accumulation was probably the most significant problem. Digester 2 had accumulated a large volume of sediment (depth of 10 – 12 ft) which greatly reduced mixing and decreased the hydraulic retention time (Figures 9 & 10). Solids accumulation appeared to be related to the composition of the flush water from the dairy housing facility and insufficient mixing. Flush water in general has very low solids content, less than one percent, while undiluted manure generally has total solids content above 10 percent (Table 1). A thickening vault was incorporated into the initial design to increase the solids content of waste pumped into the digesters, and measurements show that it did serve that purpose, although solids content were still below two percent (Table 1).

Diluted manure solids in a flush system settle much more readily than solids in undiluted manure, due to high viscosity. The composition of manure wastewater may also have

[1] Organic matter loading is based on a flow rate of thickened manure wastewater influent of 26,000 gal/d and a volatile solids (VS) concentration of 1 percent (Table 1).

contributed to this problem. Our measurements at the Fiscalini Farms Dairy AD in early 2013 showed that about 40 percent of the solids in digester influent were inorganic, also called fixed solids. Inorganic particles generally settle faster than organic particles and also are not broken down within the digester. As excreted, manure solids are typically less than 15 percent fixed solids (ASABE, 2006). Likely sources of the inorganic material in the manure wastewater included soil material and accumulation due to fiber recycling. Increases in fixed solids (from 10 to 47 percent) from the time of screening to eventual use as bedding) suggested that introduction of soil material was happening.

Table 1: Total solids, organic matter, and inorganic material in flush water and digester 1 influent at Fiscalini Farms Dairy in early 2013.

Material	Total solids (%)	Organic matter (%)	Organic matter (% of total solids)	Fixed solids (% of total solids)
Flush water	0.68	0.38	56	44
Recycled flush water	0.84	0.50	60	40
Wastewater influent	1.3	0.83	62	38
Screened fiber	19	17	90	10
New drying fiber	51	40	79	21
Old drying fiber	86	47	55	45
Clean bedding	81	43	53	47

Notes: Organic matter is measured as volatile solids (VS) at 550C. Fixed solids ("ash") is the remainder left over after combustion.

Source: UC Davis

Figure 9: Inside of digester Number 2 during the January 2013 cleanout operation.

Source: UC Davis

Figure 10: Components of the in-vessel mixing system in Fiscalini Farms digester Number 2 shown during partial cleanout in January 2013.

Source: UC Davis

Note that the propeller and lower mixing nozzle were entirely buried in 10 feet of sediment.

Low energy recovery does not directly affect the operation of the digesters but does have a major effect on economic viability. The electrical power potential from just manure on a dairy with 1,500 lactating cows, 240 dry cows, and 1,000 heifers is approximately 280 kW. As mentioned above, manure wastewater at Fiscalini Farms Dairy in early 2013 only contributed to about 20 kW of power. At 0.10 $/kWh, this difference in power generation is a missed opportunity to generate about $150,000 per year[2]. Low power generation seemed to have been primarily due to the low efficiency of solids capture—the majority of manure passed through the thickening vault and did not enter the digesters. Additionally, the soluble organic matter in manure—a component that cannot be captured with a thickening vault—is generally more degradable than the particulate material, and gram for gram, has a greater capacity for generating methane.

However, even with complete transfer of manure organic matter from all heifers and lactating/dry cows into the digesters, electricity generation would by no means approach the capacity of the system at Fiscalini Farms. With a total working volume of 1.7 million gallons, these digesters could reliably handle the manure from more than 3,000 milking cows, and produce enough biogas from this manure to generate more than 400 kW of electricity. By minimizing retention time to 20 days, these digesters could handle manure from a maximum of about 4,500 lactating cows, which could support production of about 600 kW. The capacity of the generator at Fiscalini Farms was 710 kW, a value that can only be realized by adding additional, more concentrated sources of degradable organic matter, such as food waste, a solution that had substantially been implemented by Mr. John Brenan from Organic Solutions in the first months of 2013 and that has continued ever since. A complete description of this program can be found by the companion Energy Commission report by Brenan et al. (2014).

In short, the following issues were observed and resolved:

The inorganic solids resulted from the drying methods of the digested manure solids that were subsequently used as bedding for the dairy cows. This drying process involved spreading the solids onto bare ground and then rotating them with farm implements. This practice entrained dirt and sand into the bedding. This bedding ultimately ended up going through the digestion system filling the digesters with sand and dirt.

The accumulation of sand and dirt in the digesters reduced the working volume in the digester, thereby reducing the hydraulic retention time (HRT). The reduced HRT leads to decreased digestion efficiency, lowering gas production. It also causes decreased mixing which again reduces digestion efficiency. The build-up of these solids also promotes higher concentration of sulfur-reducing bacteria, increasing the H_2S gas production. When digester 2 was removed from service it was found to have lost over 30 percent of it volumetric capacity and all four mixers were inoperable.

During sampling in late 2012 and early 2013, it was found that as much as 40 percent of the total solids were inorganic in nature. The digester was operating at less than 20 percent of its gas

[2] Assuming operation for 255 days per year.

generation design capacity. In early 2013, the digester receiving system was redesigned to preclude inorganic solids from entering the systems. This was conducted by using settling basins to remove the majority of the inorganic sand and dirt particles. Subsequent testing by Brenan showed that a large reduction of sand and dirt occurred into the anaerobic digester. The clean-up of the inorganic matter inside the digester and the above mentioned changes in management were essential first steps to allow the investigations described in the following chapters.

CHAPTER 4:
Hydrogen Sulfide Removal for the Fiscalini Farms Digester System

4.1 Summary

The anaerobic digesters (AD) at Fiscalini Farms produce biogas that contains H_2S, as do all anaerobic digesters. The biogas H_2S concentration was generally below 300 ppm, due to partial treatment with an *in-situ* biological system. However, concentrations need to be below 50 ppm to meet California engine exhaust air emission regulations for SOx emissions. This chapter reviews H_2S measurements at the Fiscalini Farms AD and CHP, discusses requirements of an H_2S removal system, and it reviews commercial options for removal or prevention of H_2S from the biogas under California conditions.

Based on solicited proposals from four companies, the most promising hardware system found was provided by MV Technologies. This company had experience in developing systems for H_2S removal from biogas in similar applications. Their iron oxide-based system included a biological component that was reported to extend the media life and result in a lower operating cost than alternatives. However, MV Technologies has been unable to provide any performance data for their system. Very limited data from a similar installation suggested that the system may have been able to provide a H_2S concentration below 50 ppm. MV Technologies did offer a performance guarantee, but the guarantee was based on cumulative H_2S removal and not biogas H_2S concentrations.

The uncertainties in the performances of various vendors and lack of a track record under comparable applications, posed a financial risk that Fiscalini Farms was unable to take, and therefore, an alternative chemical treatment route was eventually chosen as described in Chapters 5 and 6.

4.2 Hydrogen Sulfite Situation prior to 2013 and Best Available Control Technology (BACT) Requirements

Hydrogen sulfide is oxidized to SO_2 during combustion that occurs for energy recovery, and therefore, it has been assumed that digester systems contribute to SO_x pollution. Even though the SJVAPCD is required to control SOx of sources that exceed 2 lbs/per day, they base their regulation on H_2S in the inlet (pre-combustion) rather than SOx (exhaust) measurements. In other words, even though SOx in exhaust will be reduced, H_2S measured in the biogas prior to combustion are used as a predictor of exhaust SOx instead of measuring SOx directly.

The current rule is that H_2S in biogas shall not exceed 50 ppm_v (parts per million on a volume basis) assuming that this would lead to less than 2 lbs/day of SOx after combustion. The H_2S 50

ppm concentration limit for biogas is based on the "best-available control technology" (BACT[3]) principle, and not on any particular limit for SO_x emission.

The SJVAPCD calculates the 50 ppm H_2S threshold and how it relates to SO_2 as follows:

$$(50\ ft^3\text{-}H_2S)/(1{,}000{,}000\ ft^3) \times (32.06\ lb\text{-}S)/(lb\text{-}mol\ H_2S) \times (1\ lb\text{-}mol/379.5\ ft^3) \times (64.06\ lb\text{-}SO_2)/(32.06\ lb\text{-}S) \times (1\ ft^3)/(600\ Btu) \times (1\ Btu_{in})/(0.33\ Btu_{out}) \times (2{,}545\ Btu)/(bhp\text{-}hr) \times (1{,}057\ bhp) \times (24\ hr)/(day) = 2.75\ lb\ SO_2/day$$

Assumptions:

- Max Permitted Engine Output Rating: 1,057 bhp
- Engine Efficiency at Max Permitted Engine: 33 percent
- Permitted H_2S Content of Digester Gas: 50 ppm_v
- Low Heating Value of Digester Gas: 600 Btu/scf
- SOx expressed as SO_2

As discussed in Chapter 2, the Fiscalini Farms AD units were initially constructed with an *in-situ* H_2S treatment system constructed by Biogas Energy Inc., with a goal to promote H_2S oxidation by bacteria on headspace surfaces. Dairy manure digesters generally produce biogas with H_2S in the thousands of ppm_v, while this system was designed to reduce concentrations to 250 ppm. Actual values are typically below 300 ppm.

Located at the CHP unit at Fiscalini Farms, H_2S was measured in the biogas at a 15-minute interval using an in-line meter. Results that were collected before the present research commenced (six months in 2010, two months in 2011, and all of 2012) suggest that there was an upper limit of 3,000 ppm. Additionally, reported concentrations changed rapidly (in some cases by more than 2,000 ppm from one reading to the next), which raises the possibility of measurement errors. Errors notwithstanding, historic monthly H_2S concentrations in biogas at Fiscalini Farms generally had been between 200 and 400 ppm, with high variability from day-to-day and month-to-month (Figure 11). Fiscalini Farms had been operating under a regulatory variance during the time this project was conducted; however, in the future it is expected that biogas H_2S concentrations will need to be reduced below 50 ppm. To achieve this level, it will be necessary to either install an additional system for H_2S removal or implement management strategies that achieve the same goal.

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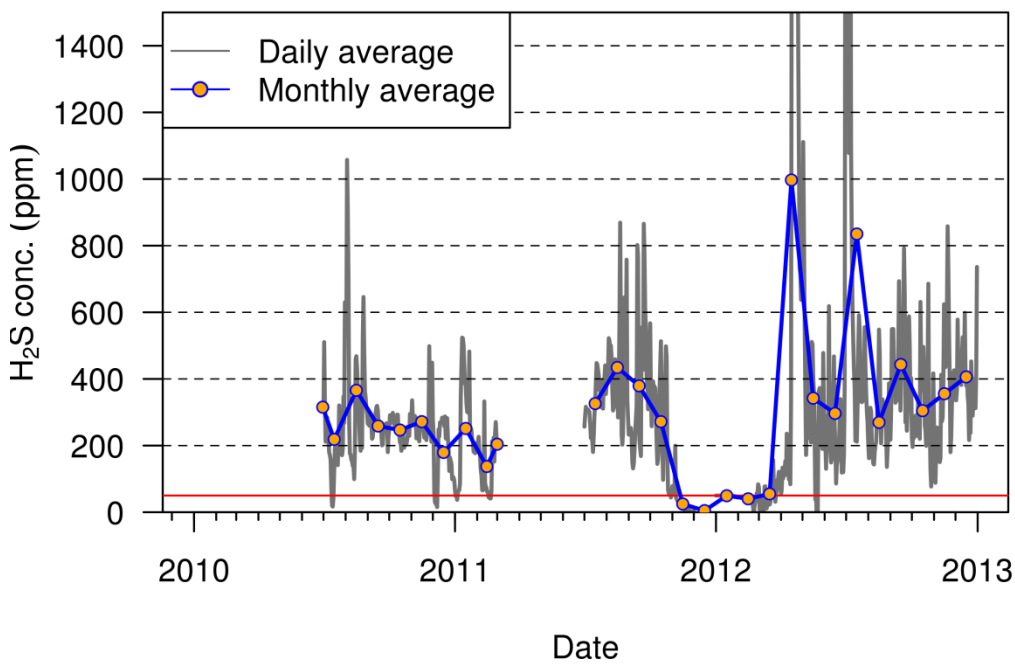
[3] The purpose of BACT is to minimize emissions from new or modified operations so they can be installed or modified without interfering with the attainment or maintenance of Ambient Air Quality Standards. In the San Joaquin Valley, any equipment requiring an air permit (boiler, engine, turbine, etc.) that is installed and has the potential to emit greater than 2.0 lbs/day of any affected air pollutant is subject to the BACT requirements of District Rule 2201 for each pollutant that exceeds 2.0 lb/day of emissions. For equipment that combusts dairy-derived biogas, sulfur oxides (SOx), and in particular SO_2, are an important pollutant of concern. Sulfur oxides are precursors to sulfur dioxide (SO_2), sulfates, and particulate matter (PM_{10} and $PM_{2.5}$).

Total H_2S flow in biogas is related to the H_2S concentration and biogas flow rate. Flow of H_2S was highly variable, but was generally been below 5 kg S/d (11 lb_m S/d). As with H_2S concentration, lack of data limited the certainty of this estimate. Reliably reducing biogas H_2S below 50 ppm will require removal of essentially all of this flow of sulfur. Biogas H_2S that flows to the engine may accumulate within the engine, accumulate in engine oil (which is intermittently replaced), or exit the engine with the exhaust. The most important sink for biogas H_2S is as SO_2 in the exhaust. Emission of exhaust SO_2 can be related to H_2S concentration and biogas flow as shown in Figure 12. The predicted SO_x emission is based on the assumption of 100 percent oxidation of H_2S to SO_x, as shown in Figure 13. In this case SO_x emission is simply twice the flow of H_2S, because the ratio of molar masses of SO_2 to S is 2.0:1.

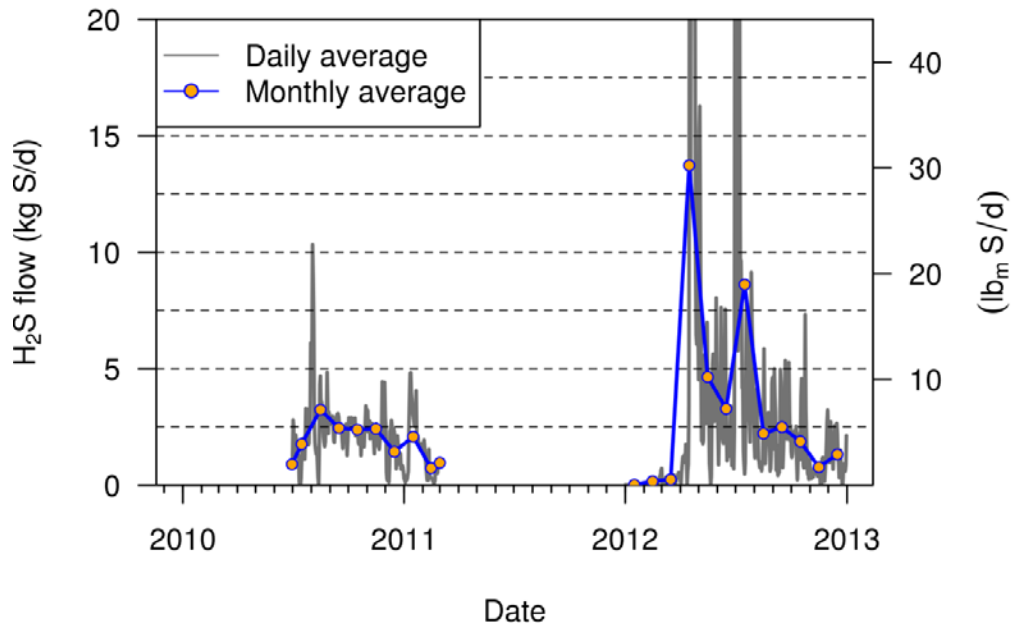
Figure 11: Concentration of H_2S in biogas from the Fiscalini Farms digesters from 2010-13, as measured by the online meter at a 15-minute interval.



Source: UC Davis

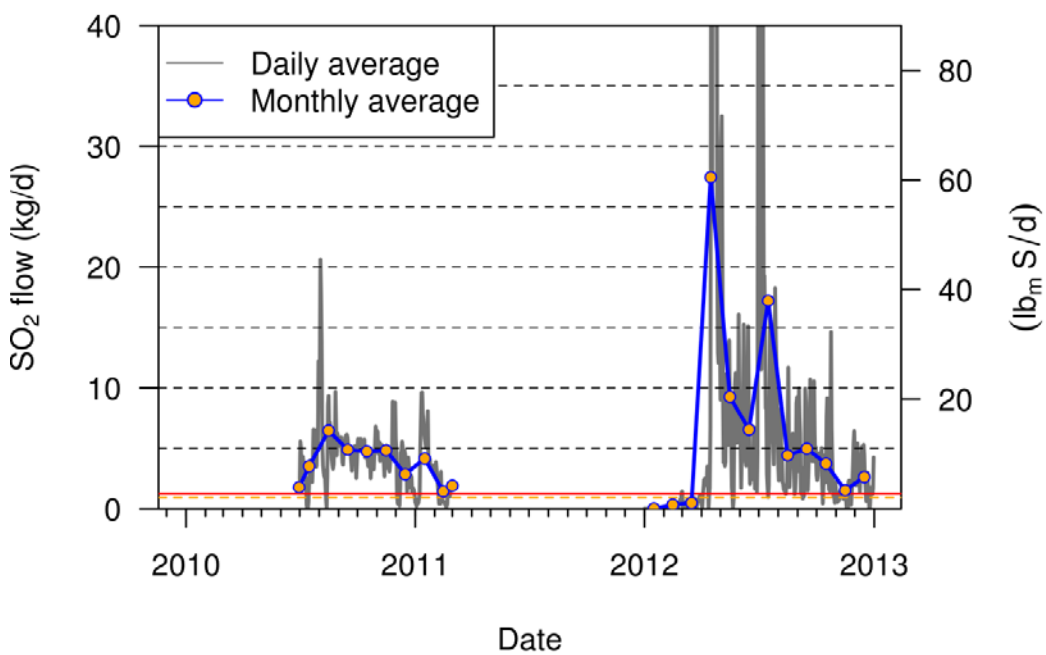
Values shown here are daily averages of the 15 minute values and monthly averages of these daily values. The solid red line shows the 50 ppm_v limit.

Figure 12: Flow of sulfur to the engine in biogas as H2S based on measurements of biogas flow and biogas H2S concentration.



Source: UC Davis

Figure 13: Predicted emissions of SOx (as SO2) in engine exhaust, assuming 100 percent conversion of biogas H_2S to exhaust SOx.



Source: UC Davis

The solid red line shows the District limit of 2.75 lb/d (1.25 kg/d), and the dashed orange line shows the BACT requirement cutoff of 2 lb/d (i.e. the level below which the BACT requirement would not apply).

4.3 Overview of 'Hardware' H_2S Removal Options for Fiscalini Farms

The most common technology in use today for H_2S removal from dairy-derived biogas and landfill gas is the iron sponge method. For this method, biogas is piped through a reactor containing hydrated ferric oxide ($Fe_2O_3 \cdot H_2O$), which is typically supported on some substrate, such as wood chips. The H_2S participates in a redox reaction with the $Fe_2O_3 \cdot H_2O$ to form pyrite and elemental sulfur, and this reaction removes H_2S from the gas stream. It has been reported that this technology is capable of keeping H_2S as low as 1 ppm in treated biogas. The basic approach has been in use for more than 100 years. Biological oxidation can also be used to remove H_2S. The Fiscalini system was designed to have biological oxidation within the digester headspace to reduce concentrations of H_2S. In theory, dedicated reactors supporting a microbial population of H_2S oxidizers can achieve greater removal.

For the present project, the UC Davis team discussed treatment options with four companies specialized in biogas cleanup: MV Technologies, SulfaTreat, Univar, and American Biogas Conditioning. These companies produced proposals based on a biogas H_2S concentration of 500 ppm and a gas flow rate of 12,500 m^3/d (300 SCFM), which is a H_2S mass of 8.4 kg S/d (19 lb S/d). Expected biogas flow was predicted based on expected power generation of 750 kW, a methane content of 65 percent, and a generator efficiency of 25 percent. Except in the case of very low generator efficiency, this biogas flow estimate will probably not be exceeded for extended periods of time. However, the above data used to determine biogas H_2S concentrations were limited, variable, and may have contained errors.

An H_2S removal system would require one or more reactors, piping, media, and, depending on the system used, possible pumps and blowers. Two of the companies, Univar and SulfaTreat, typically provided media only, but offered to assist with planning and finding of vessel manufacturers. MV Technologies and American Biogas Conditioning, on the other hand, offered to provide turn-key systems. Each of these companies proposed a single reactor, with a media volume between a little greater than 600 cubic feet (17 m^3). The capital costs for the two turn-key systems included all the components required for operation but not installation labor costs. The American Biogas Conditioning system would also have required a biogas drying system, the cost of which was not included in their estimate.

The costs of the proposed systems are summarized in Table 2. The American Biogas Conditioning system has the lower estimated annual operating cost, while the H2S Plus system by MV Technologies has the lowest capital cost and lowest estimated cost over 10 years. For the iron oxide-based systems, media replacement makes up most of the operating cost. Therefore, much lower H_2S flow in biogas could result in substantially lower operating costs than those listed in the table. Conversely, operating costs could be higher if H_2S concentration and flow are higher than the estimates used for the proposals.

Table 2: A summary of hydrogen sulfide removal options for the Fiscalini Farms digester system.

Supplier	Type	Type	Media capacity (kg/m^3)	Estimated annual operating cost	Capital cost (includes media)
MV Technologies	Turn-key	Bio-activated iron oxide (BioActive Media)	220	$7,100	$96,400
American Biogas Conditioning	Turn-key	Biological oxidation		$3,000	$207,000
SulfaTreat	Media Only	Iron oxide (410 CHP)	80	$35,000	
Univar	Media Only	Iron oxide (GC-5)	200	$19,700	

Notes: Media capacity is the mass of H_2S that can be captured with the media, and directly affects the size of the vessel and the run time between required media replacements.

Source: UC Davis

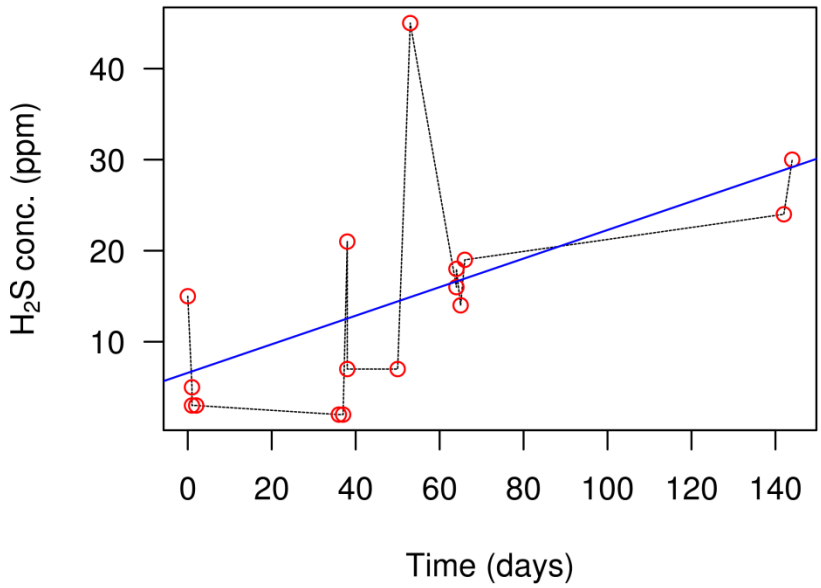
4.4 Evaluation of H_2S Hardware Removal Technologies

4.4.1 MV Technologies H2S Plus system

With the H2S Plus system by MV Technologies, the media would be replaced approximately every 13 months. Their proposal stated that the outlet H_2S concentration would be below 50 ppm_v during this 13-month "operational period". A white paper provided by the company stated that the H2S Plus system reduces H_2S to below 1 ppm_v. However, according to MV vice president of business development, Thomas Jones, because performance data were rarely collected on installed systems (apart from occasional Draeger tube measurements) he had been unable to provide any performance data from operating systems. However, our team was able to obtain 20 individual measurements for a single H2S Plus system on a California dairy.

Draeger tube measurements made for the MV Technologies system show that the original H_2S concentration in biogas was generally between 500 and 1,000 ppm. However, there appears to be a measurement limit of 1,000 ppm in the data. Cleaned biogas contained between 2 and 45 ppm of H_2S (Figure 14). These results suggest that the system was s capable of reducing H_2S below 50 ppm. However, the data also show a clear increase in H_2S concentration over time. If the observed trend continued beyond the available dates, the resulting H_2S concentration would be greater than the SJVAPCD limit of 50 ppm before the end of the first year of operation. As a result, our group concluded that it would have been improbable that the H2S Plus system can keep H_2S below 50 ppm over the proposed 13-month media life.

Figure 14: Measured H2S in biogas after scrubbing with MV Technologies H2S Plus system at a dairy manure digester system in California over time.



Source: UC Davis

Red points are measured values, and the blue line shows a linear least-squares model of H2S over time.

4.5 American Biogas Conditioning

The American Biogas Conditioning proposal stated that outlet H_2S would be between 45 and 100 ppm_v, i.e., their system will not meet the SJVAPCD limit of 50 ppm_v. A company representative, Mr. Steve McGlynn, provided a summary of the performance of three existing installations, which showed that the system would not meet the 50 ppm_v limit.

4.6 Conclusions of the H_2S Hardware Evaluation

The Fiscalini digester system needed a H_2S scrubber or alternative management strategy that could reliably reduce biogas H_2S to a concentration of 50 ppm. Of the hardware systems we reviewed, on paper, the most promising appeared to have been the H_2S Plus system produced by MV Technologies, based on cost and performance as described by the company. However, without additional performance data that clearly show that the system can consistently maintain an outlet H_2S concentration below 50 ppm for biogas with at least 500 ppm H_2S, it was not possible to recommend the system for the application at Fiscalini Farms. While installation of an H2S Plus system would certainly reduce biogas H_2S, and therefore, SO_x emission, it was not clear that H_2S would consistently be lower than 50 ppm. Instead of proceeding with the installation of an iron sponge system, the new AD system manager implemented a chemical removal system, which involves the use of FeCl applied directly into the digester, and modifications to the SCR systems were performed by Chris Weaver with EF&EE.

4.7 NOx Emissions Reduction using SCR Technology

Another criteria pollutant measured was NOx, specifically NO and NO_2. This project has demonstrated that a selective catalytic reduction (SCR) system when appropriately designed—can operate reliably and economically in a dairy-derived biogas setting. The main technical issues with the application of SCR to dairy-derived biogas are variability in engine-out NOx concentrations and the relatively high sulfur content of biogas compared to pipeline natural gas. The variation in engine-out NOx is attributable to variability in the air-fuel ratio due to biogas variability. NOx-emissions from lean-burn Otto-cycle engines are strongly affected by the air-fuel ratio. The SCR control system used for this project dealt with this variability through the use of solid-state NOx sensors upstream and downstream of the SCR catalyst. This system proved reliable and effective in controlling NOx emissions for up to at least 40,000 hours of operation. The NOx emission standard used by the San Joaquin Valley Unified APCD for permitting biogas engines is 0.15 grams of NOx per BHP-hr. This is equivalent to about 11 or 12 ppm calculated on a dry basis and corrected to 15 percent O_2. This project has shown that the APCD's permit limit is technically and economically feasible. Since this project started, at least five additional biogas-fueled engines have been permitted in the San Joaquin or Sacramento Air Districts using similar SCR technology. Four of those are operating successfully; while the fifth is scheduled to begin operation in the Spring of 2015.

The SCR catalyst employed a vanadia-titania-tungsten oxide chemistry. Unlike some other SCR catalyst formulations, this catalyst type is essentially unaffected by sulfur, so that the relatively high sulfur content of the biogas did not affect the performance of the NOx control system. Overall, the SCR system employed at Fiscalini Farms has kept the NOx levels at allowable levels.

CHAPTER 5:
Monitoring and Chemical Mitigation of Air Pollutants at Fiscalini Farms

5.1 Summary

After the settled solids were removed from Fiscalini Farms digester 2 and the mixing systems inside the digesters was repaired in early 2013, the UC Davis team monitored inlet (pre-combustion) and outlet (post-combustion) concentrations of gas compounds with emphasis of those containing sulfur, namely H_2S and SOx as well as NOx and others. Baseline gas data were monitored and consequently a chemical mitigation tool ferric chloride (FeCl) was introduced by Brenan. In 2013, we measured considerably higher inlet biogas H_2S and exhaust SOx emissions than in 2014. Indeed, the analyzer used to measure SOx and NOx, a TESTO 350 XL, did not detect any SOx in the exhaust air on 12 of the 14 sampling days in 2014. On the remaining two sampling days when SOx was detected in the exhaust stream, H_2S was present in the inlet at higher than normal concentrations. At the time of submitting this final report, efforts were still underway to conduct a mass balance for sulfur and other elements in an effort to track the fate of the sulfur that was originally contained in the inlet H_2S but then no longer in the outlet SOx. Chapter 6 contains a discussion of the potential fate of sulfur during and after the SCR process. Finally, the FeCl treatment that was applied had no measureable impact on reducing sulfur emissions.

5.2 Principle of the Measurements

The H_2S in biogas in this project was measured using a Pulsed Fluorescence SO_2-H_2S-CS Analyzer (Thermo Scientific Inc., Model TEI 450i, Franklin, MA). The TEI 450i directly measures SO_2 concentrations based on ultraviolet (UV) fluorescence spectroscopy; that is, SO_2 molecules absorb UV light at one wavelength (v1) and become excited, then decay to a lower energy state emitting UV light at a different wavelength (v2).

$$SO_2 + hv1 \rightarrow SO_2^* \rightarrow SO_2 + hv2$$

Here SO_2^* represents an excited SO_2 molecule and *hv1* and *hv2* are UV light energy at the two wavelengths of v1 and v2.

The TEI 450i uses a pulsed UV light to excite the SO_2 and detects the pulsed UV fluorescence emitted by the excited SO_2 molecules. The intensity of the UV fluorescence is proportional to the SO_2 concentrations. In order to measure H_2S, the H_2S is first converted to SO_2 at high temperatures through an H_2S convertor:

$$H_2S + \text{Heat} \rightarrow SO_2$$

When the air samples bypass the convertor, the TEI 450i readings represent the original SO_2 concentrations in air samples. When the air samples pass through the convertor, the TEI 450i measures the total sulfur (*CS*) which is a combination of the original SO_2 and H_2S.

$$CS = SO_2 + H_2S$$

The difference between the total sulfur (CS) and the original SO_2 is the H_2S concentration:

$$H_2S = CS - SO_2$$

5.3 Set-up of the Experiments

The set-up of the experiments measuring H_2S in inlet gases is shown in Figure 15. Biogas generated by the anaerobic digesters was pre-processed to substantially remove moisture prior to use as a fuel source by the engine-generator set. Biogas samples were taken directly from the biogas inlet line and analyzed in real time for chemical compositions in the UCD Mobile Agricultural Air Quality (MAAQ) lab. A photo of the UCD MAAQ lab parked by the biogas utilization building that housed the engine-generator set and austere equipment and a photo inside the MAAQ lab are shown in Figure 16.

A gas dilutor was needed to dilute raw biogas samples to a concentration that could be analyzed by the TEI 450i (10 ppm). For this project, biogas H_2S concentrations were usually close to 100 ppm and sometimes as high as a few hundred ppm. The dilutor was composed of a pump, two mass flow controllers (MFC), and a mixing chamber. A 0.2 lpm biogas sample was fed to the mixing chamber through MFC#1 and 20 lpm of ambient air was added to the mixing chamber through MFC#2. The 0.2 lpm biogas sample and the 20 lpm ambient air were mixed in the mixing chamber to dilute the H_2S concentrations. A small portion of the diluted biogas sample (about 5 lpm) was taken by the MAAQ lab for analysis and the rest of the diluted biogas sample was vented to the ambient through a venting port on the mixing chamber.

Inside the MAAQ lab, both the diluted biogas sample from the mixing chamber and the ambient air were connected to a rotary valve. The rotary valve switched between the diluted biogas sample and the ambient air and sent one of them to a manifold from where the gas analyzers took samples. The computer controlled switching timing of the rotary valve, collected data from all analyzers, displayed real-time graphs of the observational data on screen, and recorded the data on the computer hard disk.

Assuming the H_2S concentration in ambient air was C_A, the H_2S in biogas was C_B, the ambient air flow rate for dilution was F_A, the biogas sampling flow rate was F_B, and the H_2S concentration measured by TEI 450i was C_M:

$$C_M = \frac{C_A \text{ x } F_A + C_B \text{ x } F_B}{F_A + F_B}$$

The H_2S in biogas was expressed as

$$C_B = \frac{C_M \text{ x } (F_A + F_B) - C_A \text{ x } F_A}{F_B}$$

When the dilution flow rate of the ambient air was set at 20 Lpm and sampling flow rate of the biogas was set at 0.2 Lpm:

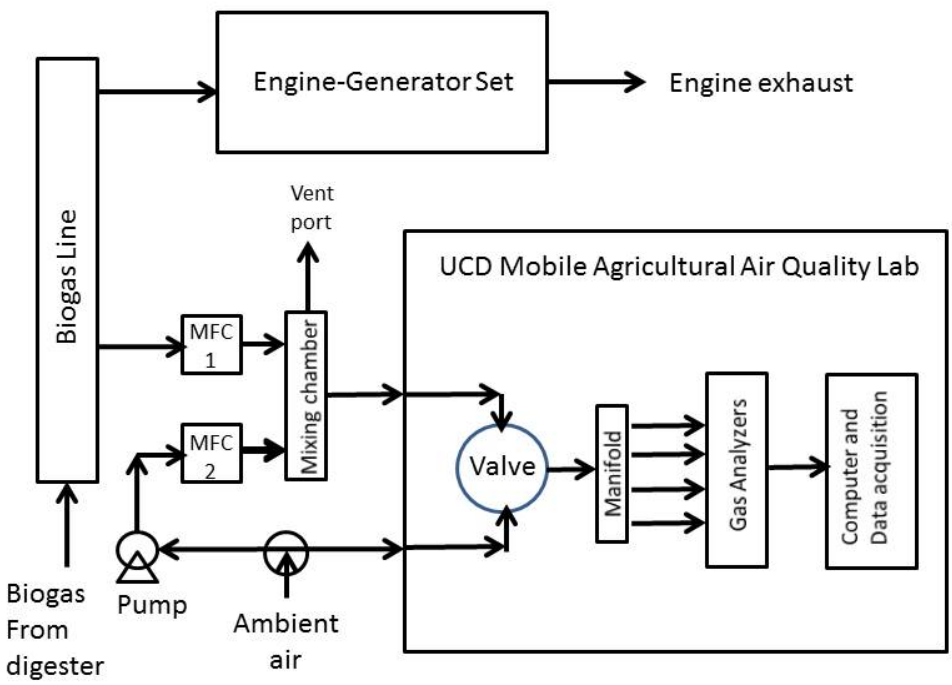
$$C_B = \frac{20.2C_M - 20.0\ C_A}{0.2}$$

If the measured H_2S is much greater than the ambient H_2S concentration (i.e. $C_M >> C_A$), the H_2S in biogas can be simplified as:

$$C_B = \frac{20.2C_M}{0.2}$$

$$C_B \cong 100\ C_M$$

Figure 15: Experimental set-up measuring H_2S in biogas pre-combustion



Source: UC Davis

Figure 16: Photos of the UCD MAAQ lab for measuring inlet gases pre-combustion. The upper photo shows the monitoring trailer and lower photo the inside of the MAAQ lab.

Source: UC Davis

5.3.1 CHP Exhaust Concentrations and Emissions

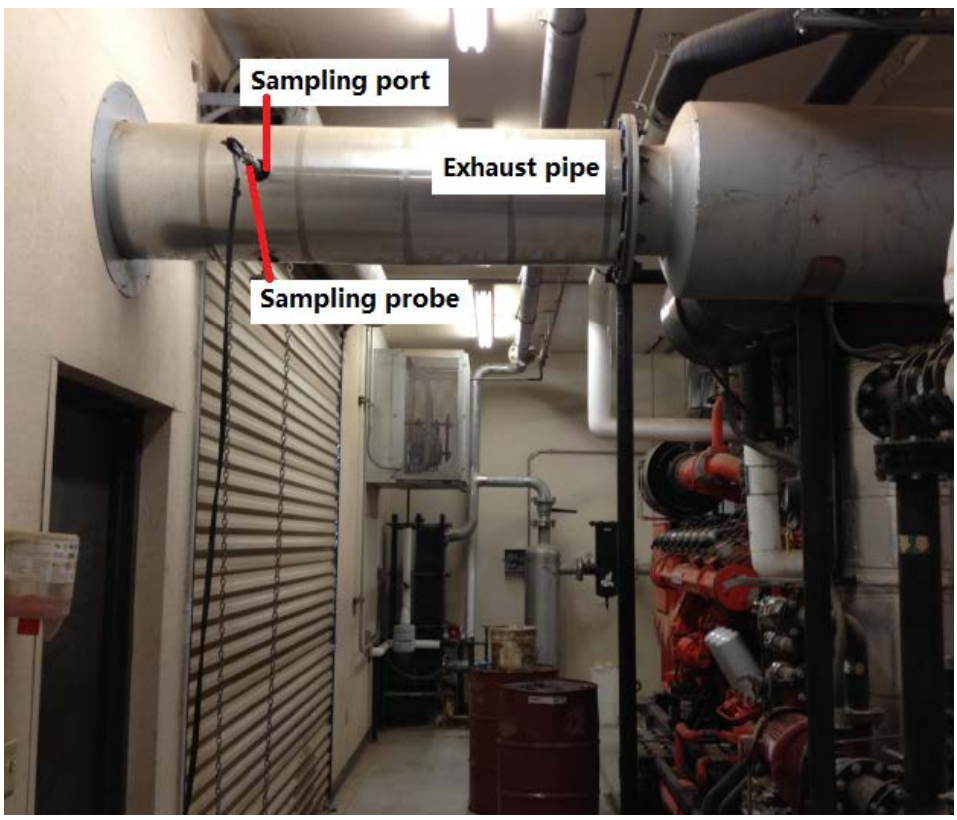
A Testo 350-XL flue gas analyzer was used to measure the engine-generator set exhaust gases (Testo, 2008). The Testo 350-XL is a portable measuring system for professional flue gas analysis and it was used by the SJVAPCD and also by the Mitloehner Air Quality Lab (separate units) as part of this project. The measuring system comprises of the control unit and the flue gas

analyzer. The Testo 350-XL was designed for assessment of industrial combustion emissions and for checking and verification of compliance with emissions requirements. The Testo analyzer used in this project had sensors to detect H_2S, SO_2, CO, nitric oxide NO, nitrogen dioxide NO_2, and O_2 (Testo, 2008). The analyzer also measured exhaust temperature, velocity and pressure. The analyzer was calibrated by the Testo Company on 3/15/2014, and challenged with standard gases during testing before it was qualified to take measurements.

During exhaust concentration measurements, the sampling probe of the Testo analyzer was inserted into the exhaust pipe through the sampling port (post-SCR, Figure 17) and the probe tip was positioned in the center of the pipe. The hot exhaust samples were drawn through a sampling tube and delivered to a condensation device to remove the water. The condensation water was collected in a container located inside the Testo analyzer. The dry air samples were then delivered into the sensors for analysis.

The Testo analyzer was programed to measure gas concentrations and automatically record data once per minute. Upon one measurement in a period, the data were saved in one file, and then the data file was downloaded by Testo Easy Emission software (Testo, 2014). The exhaust gas concentrations were tested on 16 days (Table 3) in 2013 and 2014.

Figure 17: Engine-generator set exhaust gas sample location



Source: UC Davis

Table 3: Schedule of tests for inlet and exhaust gas concentration and exhaust flow rates.

Test	Date	Inlet H_2S Concentration	Exhaust Concentration	Exhaust Flow Rate
1	8/9/2013	Yes	Yes	
2	9/13/2013	Yes	Yes	
3	3/7-4/15/2014	Yes		
4	3/24/2014	Yes	Yes	
5	3/31/2014	Yes	Yes	
6	4/15/2014	Yes	Yes	
7	5/5/-5/16/2014	Yes		
8	5/20/2014	Yes	Yes	Yes
9	8/15/2014	Yes		
10	8/18/2014	Yes	Yes	Yes
11	9/22/2014		Yes	Yes
12	9/24/2014		Yes	Yes
13	9/25/2014		Yes	Yes
14	9/26/2014		Yes	Yes
15	10/1/2014		Yes	Yes
16	10/3/2014		Yes	Yes
17	10/16/2014		Yes	Yes
18	10/23/2014		Yes	Yes
19	10/24/2014		Yes	Yes

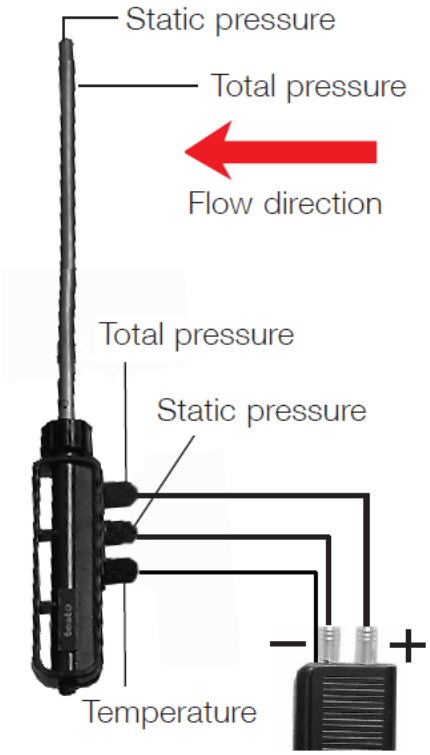
Source: UC Davis

5.3.2 Exhaust Flow Rate and Pressure Measurement

The engine-generator set exhaust gases were finally discharged through a pipe with an inner diameter of 0.3048 m (12 in). The exhaust flow rate was measured by the Testo-350-XL equipped with a straight Pitot tube. The Pitot tube can measure the total pressure and static pressure of exhaust flow using two tubes. The port of the first tube pointed directly toward the airflow to measure the total pressure, and the port of the second tube was perpendicular to the airflow direction to measure static pressure (Figure 18). The Testo reported dynamic pressure which is the differential of total pressure and static pressure. A thermocouple in the Pitot tube measured the flow temperature. The Testo reported the exhaust flow velocity and flow rates after the dimension parameters of the exhaust pipe were entered into the instrument. The Pitot tube was used to measure exhaust flow rates and total pressure of the exhaust pipe for the remainder of measurements taken

When conducting measurements, the Pitot tube probe was inserted into the sampling port (Figure 17) and maintained the probe tip at the pipe center and the total pressure port toward the flow direction. The Testo directly shows the air velocity and flow rates, which were manually recorded into the Testo analyzer.

Figure 18: Schematic of straight Pitot tube used to measure airflow rates.



Source: UC Davis

5.4 Application of Ferric Chloride to Reduce Sulfur Emissions

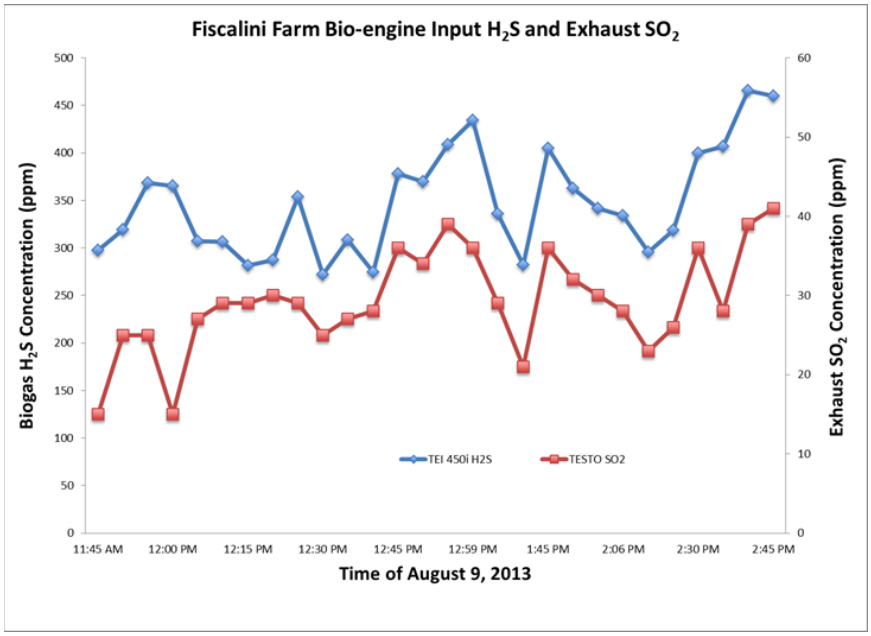
Ferric chloride was added to the each of the two digesters over two periods of time during the course of the present study with the overall goal to further reduce biogas H_2S concentrations over and above what was being achieved in the biogas head space of each digester vessel digester using a biological reduction process. Application period 1 was from 4/15 to 5/20/2014 and application period 2 was from 9/22 to 10/1/2014. During each application period 15 lbs FeCl per day was added to each digester with the initial concentration of 200 ppm FeCl being reduced to 100 ppm. The unit cost of the FeCL was reported to be $0.20 FeCl/lb delivered to the farm (Brenan, 2015) based on tote size quantities (275 gallons).

5.5 Results

The H_2S concentrations in biogas as well as SOx, NOx, and CO in the engine exhaust were measured throughout 2013 and 2014. The results of biogas H_2S concentrations and SOx in the engine-generator set exhaust are shown in Figures 19-22 as well as in Table 4.

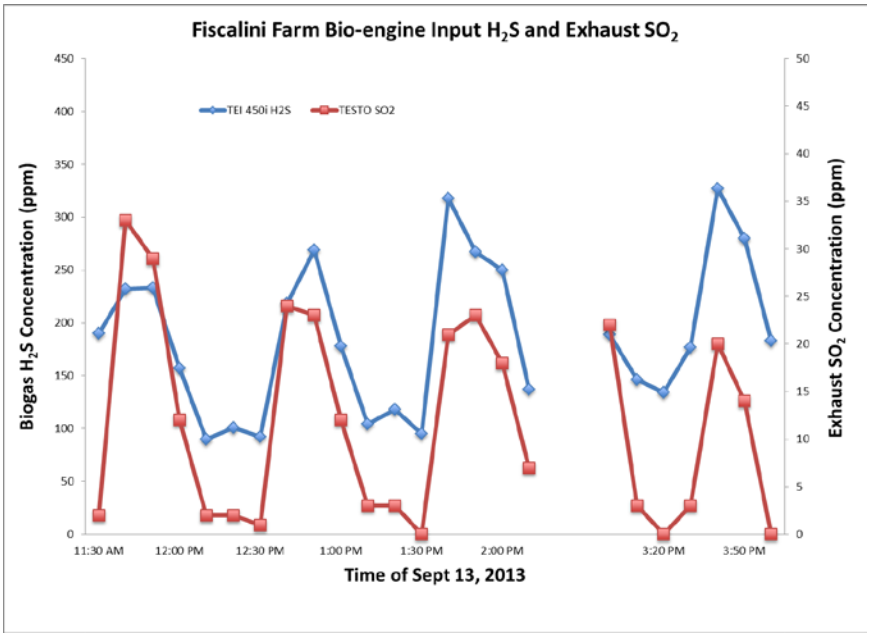
Figures 19 and 20 show H_2S and SOx following similar concentration trends, while Figures 21 and 22 show that in 2014, SOx remained at very low to zero concentrations. Tables 4a and 4b show that the addition of FeCl (see highlighted cells of the first column) did not show a consistent effect on H_2S in inlet gas. Table 4b also shows that in 2014, 12 of the 14 sampling dates yielded H_2S in the low hundred ppm range as well as zero SOx emissions.

Figure 19: Concentrations of H_2S in biogas and SO_2 in engine-generator set exhaust measured on August 9, 2013.



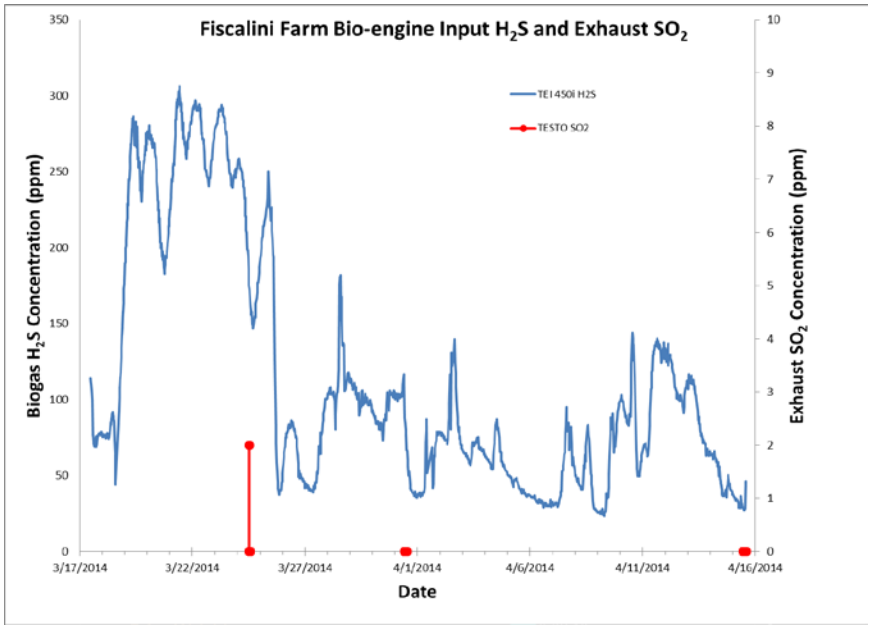
Source: UC Davis

Figure 20: Concentrations of H_2S in biogas and SO_2 in engine-generator set exhaust measured on September 13, 2013.



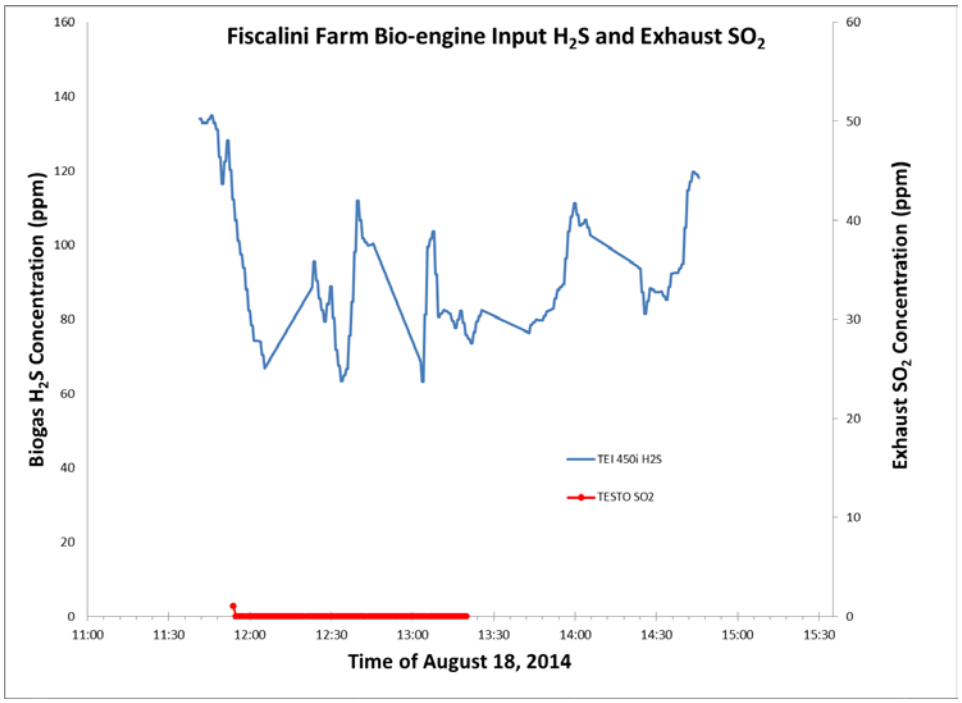
Source: UC Davis

Figure 21: Concentrations of H_2S in biogas and SO2 in engine-generator set exhaust measured between March 17 and April 15, 2014.



Source: UC Davis

Figure 22: Concentrations of H_2S in biogas and SO2 in engine-generator set exhaust measured on August 18, 2014.



Source: UC Davis

Table 4a: Summary of inlet (biogas) H_2S concentration, H_2S outlet (exhaust) concentrations, emissions, and flow rate by sampling date for 2013.

Measurement			Gen-Set Output (kWe)	FeCl App. (Y/N)	Inlet H_2S Conc. (ppm)	Outlet Concentration (ppm)						Exhaust Flow			Outlet emissions (mg/min)				
ID	Date (mm/dd/yyyy)	Duration (min)				H_2S	SO_2	NO	NO_2	CO	O_2 (%)	Flow rate (CFM)	Pres. (atm)	Temp. (F)	H_2S	SO_2	NO	NO_2	CO
1	8/9/2013	26	200	N	301	1	27	6	0	206	7	1,256	1	604	27	1,269	142	0	4,235
2	8/9/2013	29	250	N	390	1	36	8	0	213	8	1,456	1	627	30	1,916	196	0	4,967
3	8/9/2013	30	300	N	303	1	25	10	0	216	8	1,655	1	647	19	1,516	286	0	5,638
4	8/9/2013	30	350	N	398	0	32	14	0	224	8	1,855	1	662	15	2,135	424	0	6,456
5	8/9/2013	26	400	N	375	0	30	15	0	228	8	2,055	1	673	12	2,148	502	0	7,227
6	9/13/2013	60	150	N	156	0	12	8	0	90	7	1,057	1	614	9	453	144	5	1,546
7	9/13/2013	20	200	N	222	0	20	10	0	115	7	1,256	1	619	7	912	209	0	2,337
8	9/13/2013	30	250	N	159	0	7	7	0	145	7	1,456	1	644	3	354	170	0	3,339
9	9/13/2013	20	300	N	218	0	16	9	0	182	7	1,655	1	660	0	942	255	0	4,698
10	9/13/2013	30	350	N	162	0	7	5	0	208	7	1,855	1	660	4	462	149	0	6,000
11	9/13/2013	20	400	N	263	0	11	2	0	223	10	2,055	1	672	9	820	66	0	7,066

Source: UC Davis

Table 4b: Summary of inlet (biogas) H_2S concentration, H_2S outlet (exhaust) concentrations, emissions, and flow rate by sampling date for 2014. Note: blue shaded ID cells indicate when FeCl was added to the digester influent.

Measurement			Gen-Set Output (kWe)	FeCl App. (Y/N)	Inlet H_2S Conc. (ppm)	Outlet Concentration (ppm)						Exhaust Flow			Outlet emissions (mg/min)				
ID	Date (mm/dd/yyyy)	Duration (min)				H_2S	SO_2	NO	NO_2	CO	O_2 (%)	Flow rate (CFM)	Pres. (atm)	Temp. (F)	H_2S	SO_2	NO	NO_2	CO
12	3/24/2014	72	400	N	174	2	0	14	0	278	8	2,055	1	632	83	8	483	20	9,122
13	3/24/2014	28	375	N	161	2	0	16	0	283	8	1,955	1	631	59	0	531	23	8,838
14	3/31/2014	106	425	N	82	0	0	16	0	279	8	2,154	1	620	1	0	601	9	9,714
15	4/15/2014	162	500	Y	31	0	0	18	0	293	8	2,454	1	639	0	0	773	5	11,415
16	5/20/2014	33	450	Y	400	2	38	19	0	320	8	2,254	1	636	105	3,095	715	0	11,497
17	5/20/2014	35	175	Y	316	3	28	7	0	295	7	1,010	1	582	58	1,086	128	0	4,969
18	8/18/2014	24	100	N	82	0	0	14	0	272	7	854	1	552	2	0	225	0	3,995
19	8/18/2014	40	350	N	91	0	0	14	0	299	8	1,977	1	640	0	0	484	0	9,390
20	8/18/2014	53	425	N	98	0	0	19	0	299	8	2,057	1	670	0	0	646	5	9,495
21	9/22/2014	13	300	Y	408	0	0	17	0	315	7	1,712	1	641	11	0	494	0	8,542
22	9/24/2014	58	400	Y	25	0	0	19	0	292	8	1,928	1	653	0	0	628	3	8,819
23	9/24/2014	182	400	Y	46	0	0	19	0	296	8	2,054	1	652	0	0	673	4	9,552
24	9/25/2014	59	450	Y	95	0	0	19	0	312	8	2,260	1	657	0	0	725	8	11,034
25	9/26/2014	42	525	Y	160	0	0	23	0	341	8	2,879	1	659	0	0	1,097	0	15,336
26	10/1/2014	225	575	Y	225	0	0	30	0	271	8	2,681	1	656	0	1	1,350	5	11,399
27	10/3/2014	63	600	N	220	0	0	32	0	276	8	2,766	1	662	0	0	1,466	2	11,893
28	10/16/2014	25	500	N	159	0	0	36	0	282	9	2,373	1	647	0	0	1,426	1	10,583
29	10/23/2014	98	550	N	1,717	1	180	26	0	330	8	2,584	1	656	71	16,635	1,122	0	13,342
30	10/23/2014	9	500	N	1,539	0	89	30	0	312	8	2,356	1	654	11	7,507	1,179	0	11,516
31	10/24/2014	49	350	N	97	0	0	19	0	245	8	1,661	1	636	0	0	533	0	6,463
32	10/24/2014	31	300	N	97	0	0	19	0	234	8	1,483	1	629	0	0	489	1	5,554
33	10/24/2014	46	300	N	241	0	5	17	0	239	8	1,483	1	627	0	251	437	0	5,685

Source: UC Davis

CHAPTER 6: Conclusions

The present project has investigated the emissions and mitigation of criteria pollutants at a commercial dairy AD & CHP unit. All regulatory requirements have been addressed but one issue remains unsolved. While the focus of the regulatory agency in charge (i.e. the SJVAPCD) is to minimize both SOx and NOx affecting the ambient air, only NOx has been historically measured directly. The SOx exhaust emissions has been predicted by assuming that the inlet H_2S is highly correlated to SOx emissions.

We investigated options to reduce H_2S in the inlet gas (i.e. the stage before it reaches the combustion engine), and no hardware technology offered to Fiscalini Farms would have reached guaranteed reductions. However, we used a chemical additive, FeCl and found H2S in the biogas to drop below the permitted 50ppm threshold.

In addition to measuring H2S in the biogas, we measured SOx in the exhaust and we made surprising discoveries.

In 2014, measured exhaust SOx on 12 out of 14 sampling days was zero, yet at the same time, H_2S was measured (in concentrations above the permitted 50 ppm) in the biogas that fuels the engine-generator set. Of course, the conversation of mass principle applies across the engine-generator set, which means that the sulfur cannot just disappear. At this point we offer two explanations:

- The combination of the SCR system and exhaust heat-recovery was found to provide an unanticipated benefit for the control of SO_2 emissions. At intermediate temperatures, ammonia slip from the SCR system combined with SO_2 to form solid ammonium bisulfate. The exhaust heat recovery system cooled the exhaust below the ammonium bisulfate deposition temperature, thus removing both ammonia and SO_2 from the exhaust stream and depositing them in the heat-exchanger tubes. The resulting deposits can be removed easily by washing with water and the product can be useful as fertilizer. It has yet to be quantified if indeed this pathway is responsible for reducing sulfur from the gas stream leading to low SOx exhaust.
- A second explanation relates to the actual SOx measurement instrumentation. The instrument type that had been used at Fiscalini Farms by both the SJVAPCD and the UC Davis team, a Testo 350XL, yielded zero exhaust emissions on the majority of days in 2014. A co-location sampling event with two Testo analyzers (one owned and operated by the SJVAPCD staff and one by the UC Davis team), both yielded zero emissions in exhaust air. This poses the question if there might be a measurements artifact of this instrument type that causes zero readings despite SOx being present. One such artifact could be that within the Testo, the hot engine exhaust air has to be cooled down and this process generates condensate, which our research has found to collect sulfur in the liquid. It is possible, and subject to future research, that indeed some sulfur gets trapped

in the instruments condensate liquid and that some SOx never reaches the actual gas sensors within the monitor. How much this process is involved in zero readings of SOx is unknown but considering that the Testo XL is a standard monitor used across air districts throughout the US, this will be important to research to avoid costly regulation without positive effects on pollution release.

Both avenues, the deposition of sulfur post combustion in the heat exchange unit in form of ammonium bisulfate and the potential of sulfur sampling artifacts inside the Testo units, have not been described in the scientific literature and will be subject of future research.

In summary, the Fiscalini Farms AD and CHP units are now in compliance with current rules to minimize NOx and SOx and relevant precursors and at this point no additional BACT is warranted.

GLOSSARY

Term/Acronym	Definition
UC Davis	University of California Davis
AgSTAR	US EPA AgSTAR Program
ASABE	American Society of Agricultural and Biological Engineering
RD & D	Research, Development and Demonstration
BACT	Best Available Control Technology
AD	Anaerobic Digester
ADPG	Anaerobic Digester Power Generation
CHP	Combined Heat and Power
SJVAPCD	San Joaquin Valley Air Pollution Control District
MSW	Municipal Solid Waste
MW	Megawatts
MSW	Municipal Solid Waste
RPS	Renewable Portfolio Standard
GHG	Greenhouse Gas
ARB	Air Resource Board
USDA	United States Department of Agriculture
PM	Particulate Matter
SCR	Selective Catalytic Reduction
TMR	Total Mix Ration
SCR	Selective Catalytic Reduction
PPA	Power Purchase Agreement
WV	Water Vapor
RNG	Renewable Natural Gas
EF&EE	Engine, Fuel, and Emissions Engineering, Inc.

LPG	Liquid Propane Gas
VS	Volatile Solids
HRT	Hydraulic Retention Time
APCD	Air Pollution Control District
MAAQ	Mobil Agricultural Air Quality
MFC	Mass Flow Controllers

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APPENDIX A:
Benefits of Anaerobic Digestion of Dairy Manure

There are many benefits of farm-based anaerobic digestion systems that benefit farmers and non-farmers alike, thus providing substantial reason for pursuing farm-based anaerobic digestion systems. The major benefits include:

- **Odor Reduction –** Manure is commonly stored long-term (6 months or more) to reduce the chance of pollution to water bodies. Long-term storage of raw (untreated) manure releases offensive odor emissions, especially when the storage is agitated prior to empting and when applied to a farm's cropland. However, digested manure can be stored and recycled to the farm's land base with far less odorous emissions; less odor allows a farmer to be more flexible in dealing with how manure is stored and recycled to the land base.
- **Conservation of Crop Nutrients –** The anaerobic digestion process does not consume the manure nutrients nitrogen (N), phosphorus (P), or potassium (K) all of which are important for crop production.
- **Improvement in Crop Utilization of Manure Nutrients –** Effluent from digesters can be stored long-term without significant odor problems allowing farmers to apply nutrients to even sensitive field crops in an agronomic, timely fashion, thus reducing the potential for surface water and/or groundwater contamination. Additionally, the specific forms of the crop nutrients N and P are more available for use by planted crops than raw manure, thus furthering the impact of anaerobic digestion on crop production.
- **Improvement of Water Quality –** Agronomically preferred application times coincide with periods when predicted runoff and leaching is minimal thus minimizing contamination to receiving water bodies.
- **Generation of Renewable Fuel/Energy –** Biogas can be used to generate electricity and hot water and/or dry materials such as corn and cow bedding, or used in a number of other potential alternative uses that can be used on- or off-farm, including liquid fossil fuel replacement.
- **Revenue potential –** Besides reducing on-farm purchased energy costs for electricity and/or heat, the digester can facilitate other enterprises such as digested manure solids sale as compost or bedding, excess electricity sales, or co-digestion of food waste for a tipping fee.
- **Pathogen Reduction –** Cornell research has shown a 99.9 percent reduction of indicator organisms (those that are commonly used to evaluate the success of a system's performance relative to killing pathogens).
- **Reduction of Greenhouse Gas Emissions –** Cornell applied research has shown that on average for every two cows' worth of manure digested annually, one US car's worth of GHG emissions are removed. This is good for the environment and further shows consumers that farmers strive to be good environmental stewards.

- **Pre-treatment** – Anaerobic digestion produces a consistent effluent material (same temperature and pH) that is in good form for further treatment including ammonia nitrogen and phosphorus separation into discrete, usable forms for sale or on-farm use.
- **Co-digestion** – The performance of farm-based digesters is enhanced by adding off-farm substrates. Many of these substrates are costly to dispose of by other means and are not fully utilized for their energy and nutrient values.