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ANAEROBIC CO-DIGESTION PLANNING AND RESEARCH FOR GREEN BAY, WI

by

Jonathan Kusowski

A Thesis submitted to the Faculty of the Graduate School,
Marquette University,
in Partial Fulfillment of the Requirements for
the Degree of Master of Science and Engineering

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ABSTRACT
ANAEROBIC CO-DIGESTION PLANNING AND RESEARCH FOR
THE GREEN BAY METROPOLITAN SEWERAGE DISTRICT

Jonathan Kusowski

Marquette University, 2013

The aspiration to find an alternative sustainable fuel source is an ever growing concern. Anaerobic digestion might hold the answer to finding an alternative sustainable energy source. Anaerobic digestion does not only provide a renewable resource in the form of biogas, but also stabilizes wastes, preventing large amounts from being landfilled or incinerated. Anaerobic digestion of municipal wastewater sludges can often be improved by the addition of high strength industrial wastes, in a process called co-digestion. High strength industrial wastes provide an additional carbon source for the microbes to utilize and convert into usable biogas. Co-digestion also offers the opportunity for the high strength wastes to be converted to renewable energy (biogas) rather than being landfilled of incinerated. During co-digestion, the three possible outcomes are synergistic, neutral or antagonistic with respect to gas production. This study was designed to test the effects of co-digesting various high strength industrial wastes in addition to actual municipal sludge from a wastewater treatment plant. Preliminary screening of 20 industrial wastes was completed to narrow the list down to four of the most promising wastes to be used during the bench-scale study. The most promising wastes were characterized by haul distance, chemical oxygen demand (COD), Volatile Solids (VS):Total Solids (TS) and biochemical methane potential (BMP) results. A long term bench-scale study was designed to test the effect of anaerobic digestion as well as co-digestion. The bench-scale digesters were run for 275 days over four different phases. The first phase tested the effect of digesting actual municipal sludge at an organic loading rate (OLR) range of 3 to 6 gCOD/L-day. The second, third and fourth phases tested co-digestion of a consistent mix of the four co-digestates with municipal wastewater sludge at increasing organic loading rates. The OLRs increased during each phase: Phase 2 OLR (4 to 7 gCOD/L-day), Phase 3 OLR (4 to 9 gCOD/L-day) and Phase 4 OLR (6 to 10 gCOD/L-day). Phase 3 and Phase 4 tested the effect of increasing the volume of co-digestate added in an attempt to achieve the maximum OLR of the bench-scale digesters. Co-digestion during Phase 2 and Phase 3 proved to be very beneficial. Phase 2 compared to Phase 1 resulted in an increase in CH_4 production ranging from 18% to 31% as well as an increase in VSR of 6.7% to 13%. Phase 3 compared to Phase 1 saw an increase in CH_4 production ranging from 34% to 45% as well as an increase in VSR ranging from 9.4% to 23%. Phase 4 digestion proved to be near or above the maximum OLR for the bench-scale digesters, resulting in operational issues and digester failure. Co-digestion could prove to be a solution to finding an improved renewable energy, but testing on the different high strength wastes that could be used to improve this technology.

ACKNOWLEDGEMENTS

Jonathan Kusowski

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I am grateful to my parents who have provided me with advice and support throughout my graduate studies.

DEDICATION

I would like to dedicate this thesis to my family, especially my parents, whose support throughout this project and my life has made me the person I am today.

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1 Introduction and Literature Review

1.1 Renewable Energy

A continuous supply of energy is crucial for sustainability and growth of modern societies (Asif and Muneer, 2007). Presently, the majority of the world's energy is supplied by burning fossil fuels. Renewable energy could be a solution to the world's growing energy challenges (Asif and Muneer, 2007). Various renewable processes are currently being used as an alternative to burning fossil fuels. These processes include: solar, wind, biogas and wave/tidal energy, as well as other processes (Mohanty, 2011). Energy production and waste stabilization are both benefits of anaerobic digestion (McCarty, 1964). Anaerobic digestion is a stable and beneficial process that can supply renewable energy through biogas production as well as treat high strength wastes (Alatriste-Mondragón *et al*., 2006, Martín-González *et al*., 2010, Luoustarinen *et al*., 2009, Merlino *et al*., 2013).

1.2 Anaerobic Digestion

Anaerobic Digestion (AD) is a process that has been used for approximately a century to treat high-strength organic wastes while supplying energy from biogas (Merlino *et al*., 2013). Biogas produced from the process is composed of (55-75%) methane (CH_4) and (25-45%) carbon dioxide (CO_2), with trace concentrations of hydrogen sulfide (H_2S), water vapor and other constituents (de Mes *et al*., 2003). Biogas can be utilized for the production of heat, power generation and co-generation of

combined heat and power (CHP) (de Mes *et al*., 2003). The process to convert waste into methane requires several microorganisms, typically in the absence of oxygen (McCarty, 1964).

Anaerobic microorganisms can be classified into two groups with respect to oxygen tolerance: facultative (O_2) and obligate (no O_2) anaerobes (Brock and Madigan, 1991). Facultative anaerobes are able to live and grow in the presence or absence of oxygen. Obligate anaerobes only have the ability to grow in the absence of oxygen. Organisms killed by oxygen such as obligate anaerobes are also known as "strict anaerobes" (Gottschalk, 1986).

Anaerobic digestion is carried out in four main steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis (de Mes *et al*., 2003). The four steps are carried out by four different groups of microorganisms: hydrolytic bacteria, acidogenic bacteria, acetogenic bacteria and methanogenic archaea (Speece 1996; White 2000; Ecke and Lagerkvist, 2000; de Mes et al., 2003). The process is illustrated in Figure 1.1.

Hydrolysis is the first step in the anaerobic digestion process. During hydrolysis, organic matter, often containing long chain polymers in the form of fats, proteins and carbohydrates, is broken down into monomers such as amino acids, sugars, fatty acids and alcohols (Ecke and Lagerkvist, 2000; de Mes et al., 2003). The long chain polymers are broken down by bacteria that produce hydrolytic enzymes e.g., cellulases, lipases and proteases (Ecke and Lagerkvist, 2000).

Acidogensis, or fermentation, is the second step in anaerobic digestion. The hydrolyzed materials are used as substrates to form fermented products (de Mes et al., 2003). The major products are volatile fatty acids, carbon dioxide, hydrogen gas,

ammonia and sulfide (Ecke and Lagerkvist, 2000). The third step is acetogenesis, where the fatty acids are converted into hydrogen, acetate and CO_2 (de Mes et al., 2003). Acetogenesis and acidogensis can occur at the same time. In the final step, methanogensis, methanogenic microorganisms convert hydrogen and acetic acid to methane and CO_2 (Mosey, 1983; Mah, 1982).

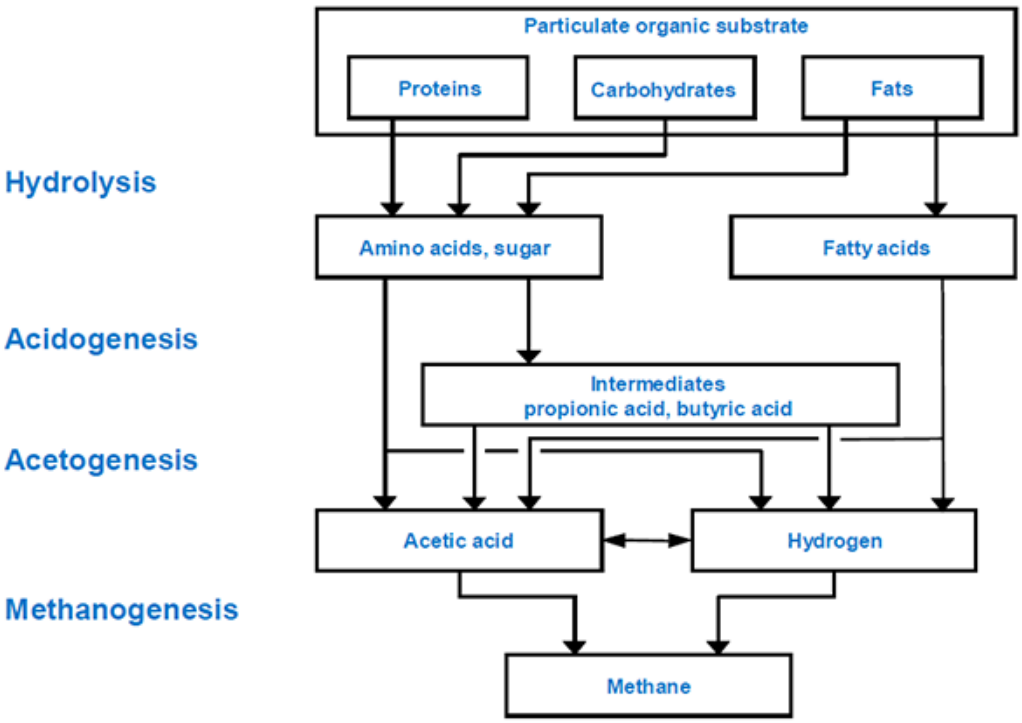


Figure 1.1: Anaerobic Digestion Process

As a result of being a biological system, certain environmental and operational factors play an important role in anaerobic digester performance. The important environmental and operating factors include: temperature, pH, mixing, hydraulic retention time (HRT), solids retention time (SRT) and reactor configuration (Karakashev

et al., 2005; McCarty, 1964; de Mes et al., 2003; Graef and Andrews, 1974, Parkin and Owen, 1986). Anaerobic digesters are often operated in the mesophilic range (30 to 38ºC or 95-105ºF) (Metcalf and Eddy, 2003). Optimum pH for methanogensis is in the range of 6.8-8.3 (Speece, 2008). Sufficient time has to be given to allow substantial destruction of volatile suspended solids (VSS) and/or chemical oxygen demand (COD), so an optimum HRT or SRT has to be employed for anaerobic digesters (Metcalf & Eddy, 2003). Mixing is another important factor for ensuring digester efficiency. Three common types of mixing include: gas injection, mechanical stirring and mechanical pumping (Metcalf & Eddy, 2003).

Anaerobic digestion is a much more attractive process for treating higher strength wastes compared to aerobic digestion, because it is more cost effective and is more efficient at stabilizing wastes (McCarty, 1964). The main cost savings are from operations because the anaerobic system does not need to be aerated (Speece, 1983). Anaerobic digestion can also handle a higher volumetric organic loading rate compared to aerobic digestion (Speece, 1983). Anaerobic digestion also offers the opportunity for energy recovery from the CH_4 that is produced (McCarty, 1964).

Sludge reduction is another advantage to anaerobic digestion compared to aerobic, because anaerobic systems produce approximately one tenth the amount of biomass as aerobic systems (McCarty, 1964; Lafitte-Trouqué and Forster, 2000). In aerobic digestion, a large amount of the energy produced when degrading material goes into forming new cells, whereas in anaerobic only a small fraction of the energy goes into producing new cells, while the rest of the energy is used to produce methane and other

byproducts(McCarty, 1964). Since only a small portion of the waste is converted to cells in anaerobic systems, the problem of disposal of excess sludge is greatly minimized.

1.3 Anaerobic Co-Digestion

A modification to the anaerobic digestion process, called "co-digestion," is being used to digest a combination of municipal and industrial wastes also referred to as co-digestates. Co-digestion is the process of combining high strength industrial organic wastes in an anaerobic digester (Totzke, 2009). In this process, the industrial wastes provide the anaerobic digesters with more degradable material resulting in higher CH_4 production. The three possible outcomes with respect to biogas productoin when co-digestion occurs are synergistic, neutral and antagonistic (Zitomer *et al*., 2008). A synergistic outcome occurs when the total CH_4 production is more when the co-digestates are combined, relative to each co-digestate digested alone. A neutral outcome occurs when the total CH_4 production is the same when the co-digestates are combined, relative to each co-digestate digested alone. An antagonistic outcome occurs when the total CH_4 production is less when the co-digestates are combined, relative to each co-digestate digested alone. Studies have been conducted on a variety of industrial wastes and the effects they have on already working anaerobic digesters (Alatriste-Mondragón *et al*., 2006). The results of some of these tests and the industrial wastes used are described below.

1.3.1 Bench-Scale Anaerobic Co-Digestion

There are many different benefits that coincide with co-digestion. In addition to an increase in CH_4 production, treatment plants could also benefit from being able to process multiple waste streams, digest poorly degradable material (for example, fat oil and grease (FOG), decrease pollution and greenhouse gas (GHG) emissions, and biologically remove toxins (Kabouris *et al*., 2009). Many different wastes have been studied to determine their potential advantages and disadvantages when added to anaerobic digesters. Some of the co-digestates and the results from pilot-scale testing are shown in Table 1.1.

1.3.2 Full-Scale Anaerobic Co-Digestion

Testing the effects of co-digestion has also been completed using existing full-scale digesters. Because often no major construction has to occur to accommodate the additional waste the co-digestates can simply be added to the existing full-scale digesters, although storage tanks, receiving facilities, and pumping equipment must be present. Some of the co-digestates and the results from full-scale testing are shown in Table 1.2.

Table 1.1: Industrial Waste Pilot-Scale Analysis

Pilot-Scale Anaerobic Co-Digestion Tests		
Synergistic	**Antagonistic**	**Neutral**
fat, oil and grease **(Kabouris et al., 2008)**	aircraft deicing fluid **(Zitomer et al., 2008)**	woody and agricultural wastes with high content of cellulose **(Converti et al., 1997)**
fat, oil and grease **(Kabouris et al., 2009)**		
Yeast waste **(Zitomer et al., 2008)**		Restaurant waste **(Zitomer et al., 2008)**
fish offal, fruit and vegetable waste, brewery sludge, dissolved air flotation **(Callaghan et al., 1999)**		molasses, chicken manure, sheep and goat manure, and fruit and vegetable waste **(Misi and Forster, 2001)**
cattle manure and milk wastes **(Callaghan et al., 1997)**		Algae **(Cecchi et al., 1996)**
agricultural and industrial wastes **(Kaparaju et al., 2001)**		carbohydrate-rich food waste **(Björnsson et al., 2000)**
hog and poultry waste **(Magbanua et al., 2001)**		
food waste **(Kim et al., 2004)**		
food waste **(Edelmann et al., 2000)**		
winery wastewater **(Rodriguez et al., 2007)**		

Table 1.2: Industrial Waste Full-Scale Analysis

Full-Scale Co-Digestion Tests		
Synergistic	**Anatagonistic**	**Neutral**
organic fraction of municipal waste, food waste and rumen content **(Kübler et al., 2000)**	human waste and domestic kitchen waste **(Yoneyama and Takeno, 2001)**	carbohydrate-rich food waste **(Björnsson et al., 2000)**
organic fraction of municipal solids waste **(Edelmann et al., 2000)**	organic fraction of municipal solid waste and municipal wastewater sludge **(Rintala and Järvinen, 1996)**	Restaurant Waste **(Zitomer et al., 2008)**
fruit and vegetable waste and sewer sludge **(Park et al., 2011)**	Aircraft Deicing Fluid **(Zitomer et al., 2008)**	Food Flavoring Waste **(Zitomer et al., 2008)**
slaughter residues **(Rosenwinkel and Meyer, 1999)**		
cow manure, confectionary byproducts and energy crops **(Kaparaju et al., 2001)**		

1.4 Synergistic, Neutral and Antagonistic Outcomes

Though many different co-digestates have been studied by themselves and in addition with other co-digestates, it is difficult to predict the outcome unless bench-scale and/or batch anaerobic bioassay tests are conducted.

Successful combinations of different types of wastes and wastewater require careful management (Navaratnam, 2012). To determine these combinations and

concentrations, bioassay testing techniques are used to test possible co-digestates. There are two bioassay tests used to identify the effects of potential co-digestates: (1) biochemical CH_4 potential (BMP) tests and (2) anaerobic toxicity assays (ATA).

1.5 Organic Loading Rates in Continuous Stirred-Tank Reactor (CSTR) Anaerobic Digesters

The typical organic loading rate of a high-rate, mesophilic, complete-mix anaerobic digester stabilizing municipal wastewater sludge at a 15- to 20-day SRT is approximately 2.3 to 6.8 grams of COD per liter of digester per day (g COD/L-day), assuming a COD/VSS ratio of approximately1.4 (Metcalf & Eddy, 2003). For design, the suggested minimum SRT for a completely mixed anaerobic digester stabilizing municipal wastewater sludge is 10 days, but the theoretical minimum can be as low as 4 days (Metcalf & Eddy, 2003). For readily degradable, rapidly acidified or soluble industrial wastewaters, such as soft drink bottling wastewater, the typical organic loading rate for a CSTR is typically less than 5 g COD/L-day. If the organic loading rate is too high, then the volatile acids concentration increases in the digester, the digester pH decreases and methanogenic organisms can be inhibited. This can lead to a decrease or stoppage of methane production. Under this condition, the digester is said to be “sour” or “stuck” and the process fails. Therefore, it is essential that the maximum sustainable organic loading rate is not exceeded.

1.6 Problem Statement

Anaerobic digestion and co-digestion have the capability of being a great alternative renewable energy resource. Increasing concern with landfilling and green house gas (GHG) emissions have encouraged more research to determine the potential of anaerobic digestion and co-digestion. In this study, research was conducted to determine the beneficial effects anaerobic co-digestion could have for an operating municipal wastewater treatment plant. Five hypotheses were tested:

1. Co-digestion allows CSTR anaerobic digesters to be operated at an OLR of 5g COD/L of digester per day or higher.
2. Co-digestion of municipal and industrial wastes increases volatile solids reduction (VSR) relative to digestion of municipal waste alone.
3. Co-digestion of municipal and industrial wastes results in higher methane production.
4. Co-digestion of municipal and industrial wastes results in a synergistic effect on digester operation.
5. Anaerobic bench-scale digesters can be run at a maximum OLR of 8g COD/L of digester, when the ratio of co-digestate OLR to the total OLR is less than or equal to 0.45.

2 Methodology

To test the effects of co-digestion, bench-scale anaerobic digesters were maintained over four phases of operation. The bench-scale anaerobic digesters were fed the same volume of primary and waste activated sludge throughout the duration of the project. Various high-strength industrial wastes within the state of Wisconsin were considered as co-digestates for the bench-scale digestion study.

2.1 Preliminary Characterization of Co-Digestates

An initial study was conducted to gather a list of suitable industrial wastes that could potentially be used for co-digestion. The criteria used to determine acceptable industrial wastes are displayed in Table 2.1.

Table 2.1: Characterization Criteria

Determining Acceptable Industrial Wastes	
Acceptable Criteria	**Unacceptable Criteria**
Liquid Form	Solid Form
Highly Degradable	Waste Requiring Special Treatment
Consistent Production Volume	Elevated Chloride Concentrations
Adequate Production Volume	Reduced Degradability
Proximity to NEW Water Treatment Plant	Odorous
Low TSS	Highly Dilute
Waste Supplier/Industry Cooperativeness	Long Haul Distance

2.3.1 Biochemical Methane Potential (BMP) Test

A BMP test is a measure of anaerobic biodegradability (Owen *et al*., 1979). A BMP test can also be used as a screening tool to test the possible toxicity of wastes, the potential inhibitory effects of a waste when mixed with the seed sludge, distinguish between biodegradable and non-biodegradable wastes, and the possible maximum CH_4 yield of a waste (Owen *et al*., 1979).

The BMP test of Owen et al. (1979) was used as one of the tools to determine the maximum expected CH_4 production from municipal sludges and industrial wastes. The seed biomass used was from a laboratory bench-scale anaerobic digester fed nutrients and non-fat dry milk. Serum bottles were seeded with 25 to 50 mL of biomass depending on the number of bottles being run. All bottles were brought to the same total volume using deionized water. Standards and the samples being tested contained approximately 65 mg COD of glucose or waste, respectively, in addition to the biomass.

The BMP tests were run using 160-mL serum bottles sparged with oxygen-free gas (7:3 v/v N_2:CO_2) after being filled with biomass and sample. The bottles were then sealed with black rubber stoppers and aluminum-crimped seals. Each BMP was run in triplicate at 35ºC and 150 rpm using an incubator shaker table (model C25KC, New Brunswick Scientific, Edison, NJ). Biogas production volume was recorded daily by measuring the displacement volume with a 100-mL glass syringe. Once recorded, the volume of biogas was injected back into the serum bottle. Once biogas production ceased, the biogas was extracted from the serum bottle and injected into 2.5 mL vials and analyzed for methane concentration using a gas chromatograph (Series 7890A GC

system, Agilent Technologies, Santa Clara, CA, USA). The maximum volume of CH_4 produced was calculated as the total volume of CH_4 produced by the samples minus the total volume of CH_4 produced by the blanks that contained seed biomass only. The BMP results were expressed as the maximum CH_4 produced divided by the initial grams of COD of the waste sample.

2.3.2 Anaerobic Toxicity Assay (ATA) Test

The ATA test was developed to determine the toxicity of a substance or waste to the microorganisms that convert acetate to CH_4 (Owen *et al*., 1979). Similar to the BMP test, the ATA test measures CH_4 production, but rather than the total CH_4 yield, the ATA test focuses on the initial CH_4 production rate (Speece, 1996). The test is set up similarly to the BMP test, but in the ATA, an identical dose of acetate is added to each bottle; a different does of the waste in questions is then added to each bottle. The ATA test is devised to test the effect of different waste doses on the rate of methane production from acetate; the results can be used to determine the concentrations of co-digestates that result in a decrease in biogas production and are, therefore toxic. Although the test was devised to determine the toxic or inhibitory affects of various materials, under some conditions, higher concentrations of materials result in higher CH_4 production rates and are, therefore, stimulatory.

An ATA test was run to determine the potential inhibitory or stimulatory effects of each co-digestate on the initial CH_4 rate when digested with calcium acetate (Owen et al., 1979). The test was set up by adding increasing concentrations of waste to a set of six serum bottles, each receiving 50 mL of seed biomass along with calcium acetate (10

g/L) as the main, non-limiting substrate. The seed biomass was from a laboratory bench-scale anaerobic digester fed nutrients and non-fat dry milk. The ATA tests were run in 160-mL serum bottles sparged with oxygen-free gas (7:3 v/v N_2:CO_2) after being filled with sample, and then sealed with solid black stoppers and aluminum-crimped seals. The tests were run at 35ºC and 150 rpm using an incubator shaker table (model C25KC, New Brunswick Scientific, Edison, NJ). Biogas volume was measured multiple times per day at ambient temperature and pressure using a 100-mL glass syringe. At the culmination of the test, linear regression was performed using the initial linear observations of cumulative biogas volume produced versus time to determine the maximum CH_4 production rate. Inhibitory effects were quantified as a waste concentration causing a 50% decreased in the CH_4 production rate (i.e., the IC_{50} concentration). Failures due to organic overload were assumed when the serum bottle content pH was below 6.8 at the end of the test.

2.2 Four Phases of Operation

In Phase 1 (control period), bench-scale digesters received only a mixture of thickened primary sludge and thickened waste activated sludge. In Phase 2 (low-load co-digestion period), bench-scale digesters continued to receive the same volume of municipal sludge, but with an additional increasing volume of industrial waste co-digestates. In Phase 3, (moderate-load co-digestion period), an increased volume of co-digestates was added to the bench-scale digesters. In Phase 4 (high-load co-digestion period) the bench-scale digesters received the largest volume of co-digestates to test for the maximum organic loading rate possible before the digesters went sour.

2.3 Identification of Most Suitable Co-Digestates

At the conclusion of the preliminary screening, the most suitable co-digestates were categorized by a biochemical methane potential (BMP) test, anaerobic toxicity assay (ATA) test, pH, average TS and VS concentrations, COD, ammonia nitrogen (NH_3-N), total Kjeldahl nitrogen (TKN) and total phosphorus (P) concentrations. The five most promising co-digestates were assayed for metal concentrations.

2.3.3 Sludge Nutrient Analysis

During Phase 1, analyses of NH_3-N, TKN, total P, total solids (TS), metals, and fat, oil and grease (FOG) concentrations were conducted by an external laboratory (Northern Lake Service, Inc., Analytical Laboratory and Environmental Services, Crandon, WI, USA). During Phase 2, analyses of NH_3-N, TKN, TP , TS and metals concentrations were conducted by the Marquette University environmental laboratory manager (Mr. Mike Dollhopf), while the FOG analysis was conducted by an outside laboratory (Northern Lake Service, Inc., Analytical Laboratory and Environmental Services, Crandon, WI, USA). Five different samples of thickened primary (TPS) and thickened waste activated sludge (TWAS) were analyzed for nutrients during Phase 1 and Phase 2. FOG testing was completed according to EPA procedures (EPA 1664M) (1999). The rest of the nutrient tests were performed according to standard methods (APHA, et al., 1998). No nutrient analysis was conducted during Phases 3 or 4.

2.3.4 Sludge Dewatering

During Phase 1 and Phase 2 steady-state, digested sludge from Digester Set D was sent out to the following dewatering equipment vendors: Andritz Separation, Inc. (Arlingtion, TX, USA), Alfa Laval, Inc. (Kenosha, WI, USA), Centrisys (Kenosha, WI, USA), Infilco Degremont, Inc. (Richmond, VA, USA) and Siemens (Holland MI, USA). Three different dewatering techniques were explored: Twist Piston Press, J-Vap Thermal Dryer and Centrifuge. The vendors dewatered the sludge using different polymers and techniques to achieve the maximum cake solids.

2.3.5 Biogas Analysis

During Phase 1 and 2 steady-state periods, Tedlar gas sampling bags collecting biogas from each reactor were closed, sealed and analyzed for siloxanes and hydrogen sulfide (H_2S) concentrations. Siloxanes concentrations were determined by an external laboratory (Analytical Solutions, Inc., Willbrook, IL, USA), by measuring the total and speciation of volatile organic silicon in fuel gases by gas chromatography-atomic emission detector. A complete description of the siloxane analysis procedure can be seen in the Appendix. H_2S concentrations were measured by Mr. Mike Dollhopf using commercial gas sampling tubes (tube number CH29101, range 100-2000 ppm, Drager, Inc., Pittsburgh, PA). Ammonia and chlorine in biogas were also analyzed using commercial gas sampling tubes (tube numbers CH20501 and CH24301, Drager, Inc., Pittsburgh, PA). No H_2S or siloxane analyses were conducted during Phases 3 and 4.

2.3.6 Analytical Methods

TS, VS, TSS, VSS, COD, soluble chemical oxygen demand (sCOD), NH_3-N, TKN, total P and alkalinity concentrations were measured using standard methods (APHA et al., 1998). The pH was measured using a pH probe and meter (Orion 4 Star, Thermo Scientific, West Palm Beach, FL, USA). Biogas CH_4 content and volatile fatty acid (VFA) concentrations were measured using a gas chromatograph (Series 7890A GC system, Agilent Technologies, Santa Clara, CA, USA).

2.4 Bench-Scale Anaerobic Digesters

Seven lab-scale anaerobic digesters were operated. Six digesters (Digesters 1A, 2A, 1B, 2B, 1C and 2C) were constructed of a transparent acrylic cylinder having a 14-cm internal diameter and 30-cm height. The top and bottom of each digester was sealed with plates made of the same acrylic material. The total volume of the digesters was 4.5-L with a working liquid volume of 2-L that was held constant throughout the duration of the study. Magnetic stir bars and stir plates were used to keep the digesters completely mixed. All six 4.5-L digesters had a total of three ports in the lid: one was sealed off, the second was used to extract digested sludge/add feed and the third was used for biogas collection. The biogas produced was collected in 5-L, 12-inch by 12-inch, polyvinyl fluoride film (PVDF) gas sampling bag (Laboratory Products Association, Fairfax, VA, USA). A schematic diagram of the 4.5-L digesters is shown in Figure 2.1.

The seventh anaerobic digester (1D) was operated to provide an adequate volume of digested sludge for shipment to dewatering equipment vendors. The seventh digester

was a 20-L vessel with a 15-L working volume, mechanically stirred using a laboratory mixer (Model 50002-30, Cole-Parmer, Vernon Hills, IL, USA) regulated by a speed controller (Masterflex, Cole-Parmer, Vernon Hills, IL, USA). There were four active ports, three on top and one at the bottom of the digester. The first top port was plugged and sealed to prevent biogas from leaking, the second was used to add feed material and the third was used for biogas collection. The fourth port, located at the bottom of the digester, was used to collect the digested sludge.

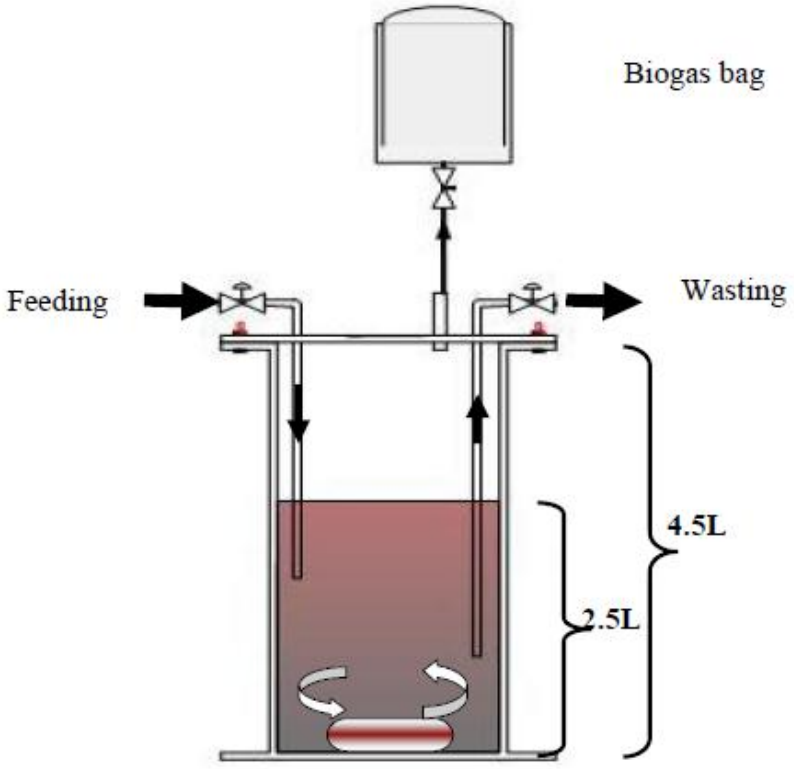


Figure 2.1: Diagram of Bench-Scale Anaerobic Digester

2.4.1 Phase 1, No Co-Digestion (OLR 3-6g COD/L of digester)

The seven digesters (1A, 2A, 1B, 2B, 1C, 2C and 1D) were initially seeded with biomass from an operating full-scale, municipal anaerobic digester at the Fox River Water Reclamation District (Brookfield, WI). Immediately following seeding, each digester was sparged with oxygen-free gas (7:3 v/v N_2:CO_2) and sealed so mixing could begin. The digesters were run in a temperature-controlled room with an average temperature and standard deviation of (34 ± 1^0C) and continuously mixed. The six bench-scale digesters were continuously mixed with magnetic stir bars (300 rpm), whereas the seventh digester (1 D) was mixed with a propeller mixer on a speed-controlled motor. During the first day of operation, the digesters were not fed, but the temperature and pH were monitored. Over the next nine days of operation, the digesters were fed at 25, 50 and 75% for three days each of the Phase 1 loading rate, while the pH and temperature were monitored. Digesters 1A and 1B were subsequently operated at 10-day SRT, whereas Digester 2A and 2B were operated at a 15-SRT, and Digesters 1C and 2C were operated at a 20-day SRT. The mixed sludge substrate (TS = 4.30% and VS = 3.38%) was a combination of municipal TPS (TS = 3.57% and VS = 2.68%) and TWAS (TS = 5.27% and VS = 4.36%) mixed at a ratio of 45:55 (TWAS:TPS), respectively, based on TS concentration. The TPS and TWAS was shipped weekly from the City of Green Bay to the Marquette University Water Quality Center and analyzed for TS, VS, COD and sCOD concentrations.

A wet test gas meter (Scientific Petroleum Instrument, San Antonio, TX, USA) was used to measure the volume of biogas collected each day in the gas sampling bag

from each digester (initially every other day, but daily once biogas volumes reached >2.0 L/day).

For Phase 1, the 10-day SRT (1A and 2A), the 15-day SRT (1B, 2B and 1D) and the 20-day SRT (1C and 2C) were fed only the blend of municipal wastewater sludge until reaching quasi-steady state (after 3 SRTs). Prior to reaching quasi-steady state, weekly analytical tests were conducted. The analytical tests and frequencies are presented in Table 2.6.

2.4.2 Phase 2, Co-Digestion (OLR 4-7g COD/ L of digester)

After day 119, all seven digesters were fed a mixture of the four industrial wastes (see Table 2.3), in addition to municipal wastewater sludge. The co-digestate mixture was comprised of the four most promising industrial wastes (see Table 2.2): Milk Processing Wash Water (COD= 26±6 g/L, TS=1.36%, VS=1.14%), Cheese Production Dissolved Air Flotation (DAF) Sludge (COD=61±37 g/L, TS=5.51%, VS=3.79%), Cheese Production DAF Sludge and Float (COD=26±11 g/L, TS=2.81%, VS=2.20%) and Vegetable Blancher Water (COD=28±10 g/L, TS=3.24%, VS=2.64%). The co-digestate blend was mixed according to the four co-digestates TS/VS concentrations as well as the TPS and TWAS TS/VS concentrations to achieve a desired VS loading rate. The ratio and loading rates of the co-digestates were based on the expected production volumes of industrial wastes that NEW Water would be receiving from each facility daily. All seven digesters were fed the same ratio of co-digestates, but different volumes (see Table 2.3). The digesters were operated until reaching quasi steady-state (3 SRTs). Prior to reaching quasi steady-state, analytical tests were conducted weekly (see Table

2.6). Once reaching quasi steady-state, analytical tests were conducted on the effluent of a set of duplicate digesters over a two-week period (see Table 2.6).

Table 2.2: Co-Digestate Analytical Results

Parameters	Co-digestate 1 (Vegetable Blancher Water)		Co-digestate 2 (Milk Processing Wash Water)		Co-digestate 3 (Cheese Production DAF Tank Sludge and Float)		Co-digestate 4 (Cheese Production DAF Tank Sludge)	
	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
COD (g/L)	23	13	27	6.3	27	12	60	38
Total Phosphorus (mg/L)	160	-	51	-	350	-	310	-
NH3-N (mg/L)	100	-	8	-	59	-	20	-
TKN (mg/L)	770	-	750	-	3,100	-	1,300	-
pH	6.2	0.34	9.3	1.1	6.3	0.42	4.4	0.2
TS (%)	2.6	1.6	1.5	0.29	2.9	1.7	4.7	2.7
VS (%)	1.7	1.0	1.3	0.32	2.3	1.5	3.2	2.4

Table 2.3: Phase 2 Co-Digestate Feed Volumes (mL/day)

	Co-digestate 1 (Vegetable Blancher Water)		Co-digestate 2 (Milk Processing Wash Water)		Co-digestate 3 (Cheese Production DAF Tank Sludge and Float)		Co-digestate 4 (Cheese Production DAF Tank Sludge)	
	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
Digester Set A	22	4	16	8	14	7	7	3
Digester Set B	11	7	11	5	9	4	5	2
Digester Set C	9	5	8	4	7	3	3	2

2.4.3 Phase 3, Increased Co-Digestion Loading (OLR 4-9g COD/L of digester)

After day 210, all seven digesters were fed an increased volume of the co-digestate mixture, in addition to the municipal wastewater sludge mixture. The co-digestates were mixed according to the four co-digestates TS/VS concentrations and the TPS and TWAS TS/VS concentrations. All seven digesters were fed the same mix ratio of co-digestates, but larger volumes than were fed during Phase 2 (see Table 2.4). The volumes of co-digestates added during Phase 3 were increased to three times those added

during Phase 2 in an attempt to reach or exceed the maximum OLR possible before the digesters went sour. The digesters were run until reaching quasi-steady state (3 SRTs). Prior to reaching steady-state, analytical tests were conducted weekly (see Table 2.7). Once reaching steady-state, analytical tests were conducted on the effluent of each set of digesters over a two-week period (see Table 2.7).

Table 2.4: Phase 3 Co-Digestate Feed Volumes (mL/day)

	Co-digestate 1 (Vegetable Blancher Water)		Co-digestate 2 (Milk Processing Wash Water)		Co-digestate 3 (Cheese Production DAF Tank Sludge and Float)		Co-digestate 4 (Cheese Production DAF Tank Sludge)	
	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
Digester Set A	68	13	38	7	33	6	17	3
Digester Set B	49	9	25	2	22	4	11	2
Digester Set C	34	7	19	4	16	3	8	2

2.4.4 Phase 4, Maximum Co-Digestion OLR and Digester Failure (OLR 6-10g COD/L of digester)

After day 253, all seven digesters were fed an increased volume of the co-digestate mixture, in addition to the municipal wastewater sludge mixture. The co-digestate blend was mixed according to the four co-digestates TS/VS concentrations and the TPS and TWAS TS/VS concentrations. All seven digesters were fed the same mix of co-digestates as in Phase 2 and Phase 3, but different increased volumes (see Table 2.5). The volumes added were estimated to be near or above the maximum OLR for the bench-scale anaerobic digesters. The digesters were run until reaching quasi-steady state (3 SRTs). Prior to reaching steady-state, analytical tests were conducted (see Table 2.7). Once reaching steady-state, digester operation ceased.

Table 2.5: Phase 4 Co-Digestate Feed Volumes (mL/day)

	Co-digestate 1 (Vegetable Blancher Water)		Co-digestate 2 (Milk Processing Wash Water)		Co-digestate 3 (Cheese Production DAF Tank Sludge and Float)		Co-digestate 4 (Cheese Production DAF Tank Sludge)	
	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
Digester Set A	64	33	39	14	33	12	63	59
Digester Set B	73	30	44	16	38	13	70	66
Digester Set C	65	34	40	13	35	12	64	59

Table 2.6: Phase 1 and Phase 2 Analytical Testing Schedules

Parameter	Phase 1, Pre Steady-state	Phase 1, Steady-state	Phase 2, Pre Steady-state	Phase 2, Steady-state
Temperature	1/Day	1/Day	1/Day	1/Day
Biogas volume produced	1/Day	1/Day	1/Day	1/Day
Biogas methane content	2/Week	5/2 Weeks	2/Week	5/2 Weeks
Intermediate and partial alkalinity	2/Week	5/2 Weeks	2/Week	5/2 Weeks
TS*	2/Week	5/2 Weeks	2/Week	5/2 Weeks
VS*	2/Week	5/2 Weeks	2/Week	5/2 Weeks
Chemical oxygen demand (COD)*	1/Week	5/2 Weeks	1/Week	5/2 Weeks
Soluble chemical oxygen demand (sCOD)*	1/Week	5/2 Weeks	1/Week	5/2 Weeks
Individual and total VFA*	2/Week	5/2 Weeks	2/Week	5/2 Weeks
Total suspended solids**	--	--	1/2Week	1/2Week
Volatile suspended solids**	--	--	1/2Week	1/2Week

*-parameters were also measured for TPS, TWAS, feed and co-digestates
**-parameters were only measured for co-digestates

Table 2.7: Phase 3 and Phase 4 Analytical Testing Schedules

Parameter	Phase 3, Pre Steady-state	Phase 3, Steady-state	Phase 4, Pre Steady-state	Phase 4, Steady-state
Temperature	1/Day	1/Day	1/Day	1/Day
Biogas volume produced	1/Day	1/Day	1/Day	1/Day
Biogas methane content	2/Week	5/2 Weeks	3 Times	3 Times
Intermediate and partial alkalinity	2/Week	5/2 Weeks		
TS*	2/Week	5/2 Weeks	3 Times	3 Times
VS*	2/Week	5/2 Weeks	3 Times	3 Times
Chemical oxygen demand (COD)*	1/Week	5/2 Weeks		
Soluble chemical oxygen demand (sCOD)*	1/Week	5/2 Weeks		
Individual and total VFA*	2/Week	5/2 Weeks	3 Times	3 Times
Total suspended solids**	--	--	1/2Week	
Volatile suspended solids**	--	--	1/2Week	

*-parameters were also measured for TPS, TWAS, feed and co-digestates
**-parameters were only measured for co-digestates

2.5 Statistical Analysis

Statistical analysis was run on data from the same digester comparing different phases of operation as well as analyzing the data of duplicate digesters to determine if a

statistical difference was present. Statistical tests were run on data from the same digesters. Different phases of operation were subject to a student t-test run in Excel as a two tail, type I test. Analysis of duplicate digesters during the same phase of operation was first subject to an F-test, in which the test statistics have an F-distribution under the null hypothesis. If the F-test resulted in a P value less than or equal to 0.05 then a two-tail type 3 student t-test would be run to analyze the duplicate digester data. If the F-test resulted in a P value greater than or equal to 0.05 then a two-tail type 2 student t-test would be run to analyze the duplicate digester data.

3 Results and Discussion

The results for identification of co-digestates, selection of co-digestates for further testing, and Phases 1 through 4 co-digestion testing are discussed in the following sections.

3.1 Identification and Classification of Most Suitable Co-Digestates

A total of 20 industrial wastes were identified for possible use in co-digestion after a survey was sent out to facilities in the treatment plant area. All of the facilities contacted were located within a 30-mile radius of the treatment plant. The wastes collected at the facilities were food, dairy, brewery, and waste treatment residuals. The industrial wastes were categorized by haul distance, flow rate anticipated, pH, average TS and VS concentration, average COD, average NH_3-N, average TKN and average total P concentrations, as well as the company cooperativeness (see Table 3.1). From the original 20 wastes, five were chosen for further analysis. The primary criteria used to choose the five most suitable wastes were: high COD, high VS content[1] and high/consistent production volumes.

3.1.1 Co-Digestate Characterization

The five industrial wastes chosen were subject to additional characterization testing (see Table 3.2). The list of industrial wastes was narrowed down to four co-digestates (Cheese Production DAF Tank Sludge, Cheese Production DAF Tank Sludge

[1] Wastes having a VS concentration over 80 % were only considered, with the exception of Milk Processing Wash Water.

and Float, Milk Processing Wash Water and Vegetable Blancher Water) for use in co-digestion. The four co-digestates chosen were used throughout the remainder of the project.

Table 3.1: Co-Digestate Analytical Results

Co-digestate description	Average COD (mg/L)	Daily Production		Average %TS	Average %VS	Haul Distance to NEW Water (miles)	pH	Average NH_3-N (mg/L)	Average TKN (mg/L)	Average TP* (mg/L)
		Amount	Unit							
Filter cake solids	2,000,000	--	--	10	8.1	6.5	N/A	140	46,000	9,600
High acid solids	1,400,000	--	--	9.9	9.1	6.5	N/A	780	31,000	4,200
Anaerobic contact WAS	240,000	9.3	wet tons	19	15	4.7	N/A	4,900	71,000	10,000
Paunch manure	240,000	33	wet tons	29	26	4.7	N/A	450	11,000	3,100
Primary wastewater sludge	160,000	--	--	11	9.4	6.5	5.9	11,000	50,000	3,200
Beer	110,000	64	gal	3.0	2.2	0.4	6.8	380	25,000	4,700
Cheese Production DAF Tank Sludge	110,000	5,500	gal	10	8.0	21	3.9	630	14,000	4,600
Somat Sludge	90,000	--	--	7.6	6.7	6.5	N/A	8,400	130,000	11,000
Vegetable Blancher Water	66,000	5,000	gal	5.7	4.8	19	6.6	400	13,000	3,700
Cheese Production DAF Tank Sludge and Float	38,000	11,000	gal	2.8	2.2	25	6.2	1,100	43,000	14,000
Pepper/pickle solids	38,000	--	--	5.8	3.4	2.8	4.1	1,200	23,000	2,700
Milk processing sour cream: Sample 2	30,000	13,000	gal	1.1	0.78	8.7	12	TBD	TBD	TBD
Milk Processing Wash Water	26,000	13,000	gal	1.2	0.94	8.7	12	TBD	TBD	TBD
Irrigation field corn	21,000	5,000	gal	0.98	0.83	19	4.5	700	82,000	7,900
Wastewater hole	15,000	8,500	gal	12	1	27	6.8	3,200	22,000	8,500
Cheese Wash Water	7,900	100,000	gal	0.69	0.52	10	9.7	4,000	19,000	8,100
Holding cell	7,400	8,500	gal	0.60	0.32	27	6.1	13,000	45,000	14,000
Cheese water (high chlorides)	6,800	19,000	gal	2.4	0.33	10	5.8	TBD	TBD	TBD
Primary wastewater water	5,700	--	--	2.3	0.26	6.5	6.7	29,000	42,000	1,300
Ridge and furrow	1,800	8,500	gal	0.37	0.13	27	7.9	7,700	ND	18,000

*TP is Total Phosphorus

Table 3.2: Four Co-Digestates - Characterization Test Results

	1		2		3		4	
	Vegetable Blancher Water		Milk Processing Wash Water		Cheese Production DAF Tank Sludge and Float		Cheese Production DAF Tank Sludge	
Parameters	**Average**	**STDEV**	**Average**	**STDEV**	**Average**	**STDEV**	**Average**	**STDEV**
COD (mg/L)	23,000	13,000	27,000	6,300	27,000	12,000	60,000	38,000
sCOD (mg/L)	18,000	9,500	8,800	1,400	1,500	1,300	20,000	15,000
TS (%)	26	16	1.5	0.29	29	17	47	27
VS (%)	17	10	1.3	0.32	23	15	32	24
VS/TS (%)	65.0	65	87	--	78	--	67	--
TSS (mg/L)	4.6	6.2	5.4	3.4	25	15	14	13
VSS (mg/L)	2.6	3	4.4	2.8	22	14	13	12
pH	6.2	0.34	9.3	1.1	6.3	0.42	4.4	0.2
Total Phosphorus (mg/L)	160	--	51	--	350	--	310	--
NH_3-N (mg/L)	100	--	8	--	59	--	20	--
TKN (mg/L)	770	--	750	--	3,100	--	1,300	--
Oil and Grease (mg/L)	9	--	1,400	--	12	--	96	--
Alkalinity (mg/L as $CaCO_3$)	810	--	1,100	--	900	--	160	--
BMP (ml CH_4/gCOD)	310	3.6	210	6.2	200	36	280	16
ATA	IC_{50}>8%	--	IC_{50}>8%	--	IC_{50}>8%	--	IC_{50}=4%	--
Beryllium (µg/L)	19	--	2	--	5	--	1	--
Sodium (µg/L)	61	--	620	--	1,600	--	6,400	--
Magnesium (µg/L)	300	--	24	--	33	--	88	--
Aluminum (µg/L)	17,000	--	14,000	--	110,000	--	23,000	--
Potassium (mg/L)	1,700	--	140	--	170	--	400	--
Calcium (mg/L)	120	--	140	--	380	--	800	--
Chromium (µg/L)	120	--	130	--	58	--	190	--
Mangenese (µg/L)	470	--	36	--	110	--	140	--
Iron (mg/L)	7	--	2	--	7	--	19	--
Cobalt (µg/L)	41	--	10	--	55	--	41	--
Nickel (µg/L)	530	--	58	--	38	--	73	--
Copper (µg/L)	730	--	430	--	560	--	900	--
Zinc (µg/L)	5,200	--	3,200	--	980	--	1,300	--
Arsenic (µg/L)	16	--	3	--	3	--	3	--
Selenium (µg/L)	34	--	70	--	11	--	10	--
Molybdenum (µg/L)	45	--	8	--	12	--	16	--
Silver (µg/L)	34	--	14	--	33	--	21	--
Cadmium (µg/L)	40	--	51	--	7	--	22	--
Mercury (µg/L)	93	--	15	--	21	--	34	--
Lead (µg/L)	200	--	240	--	220	--	240	--
Quantity (gal/day)	5,000	--	13,000	--	11,000	--	5,500	--
Distance (miles)	19	--	9	--	25	--	21	--

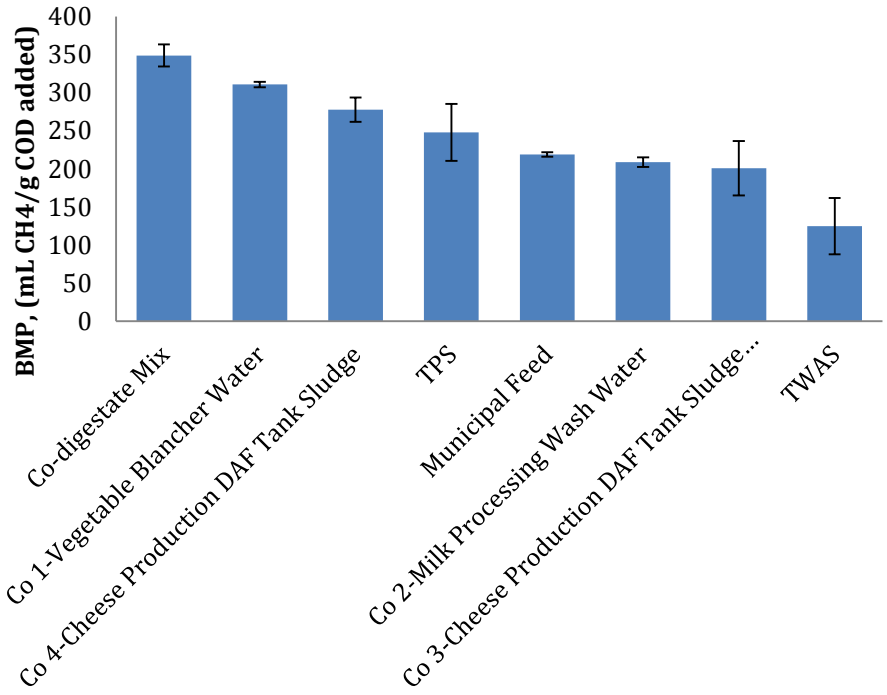
3.1.2 Co-digestate Biochemical Methane Potential (BMP) Results

Two types of BMP tests were conducted to estimate the potential maximum CH_4 yields when the co-digestates were digested alone and when the co-digestates were digested with the municipal wastewater sludge mixture. In synergistic situations, industrial wastes have the potential to increase CH_4 yield when digested with municipal wastewater sludge.

The first type of BMP tests were run using only one waste in each test setup; these tests were performed to estimate the CH_4 yielded when each of the four co-digestates or municipal wastewater sludge were digested alone (see Figure 3.1). The CH_4 yield for the co-digestates varied from 201 to 311 mL CH_4/g COD. The co-digestate mix, Cheese Production DAF Tank Sludge and Vegetable Blancher Water resulted in the highest CH_4 yields, while the Cheese Production DAF Tank Sludge and Float and Milk Processing Wash Water yielded more CH_4 than the TWAS, but not the TPS.

The second type of BMP tests were run using a mix of one industrial waste and municipal wastewater sludge in each test setup; these tests were performed to estimate the CH_4 yielded when each of the four co-digestates was co-digested with municipal wastewater sludge in a 1:1 industrial waste:municipal wastewater sludge COD mix (see Figure 3.2). Synergistic and neutral outcomes were observed when co-digestates and municipal feed sludge were digested together. Synergistic and neutral outcomes were determined by comparing the theoretical CH_4 yield to the observed CH_4 yield. The theoretical CH_4 yield (see Figure 3.2), was calculated as the sum of 50% of the municipal wastewater sludge BMP value and 50% of the co-digestate BMP value (see Figure 3.1).

The Milk Processing Wash Water was the only co-digestate that resulted in a synergistic outcome when digested with municipal sludge, whereas the three other co-digestates and co-digestate mixture resulted in statistically neutral outcomes.



n=3
error bars = standard deviation

Figure 3.1: Individual BMP Results

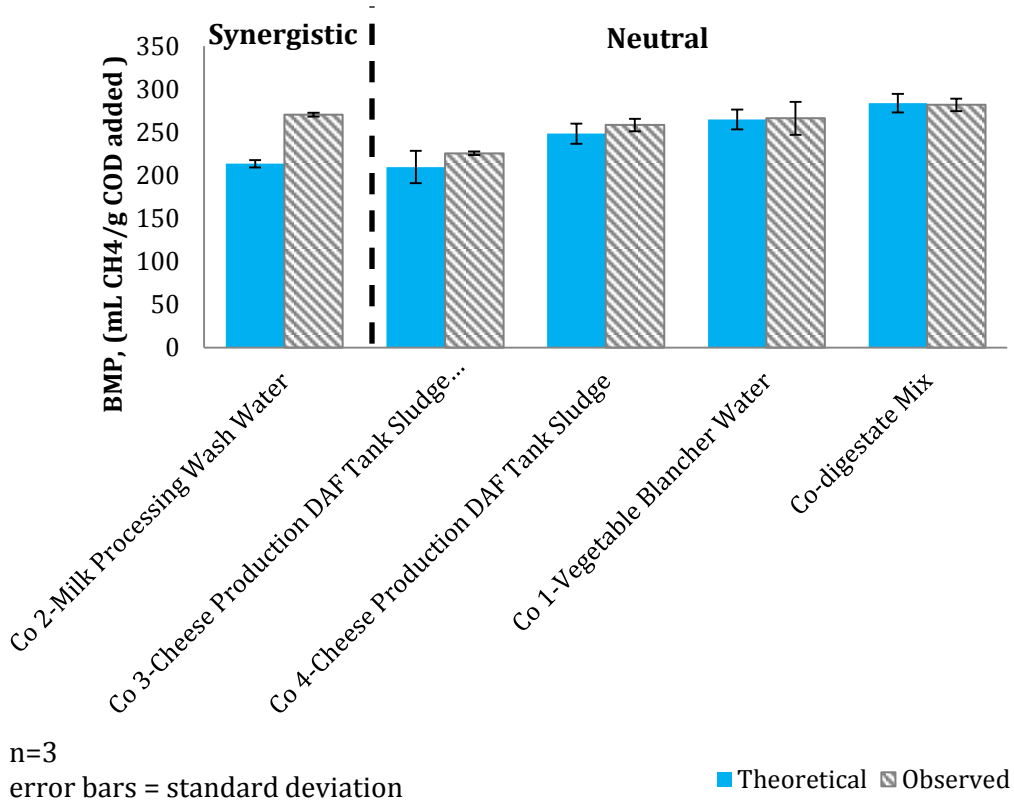
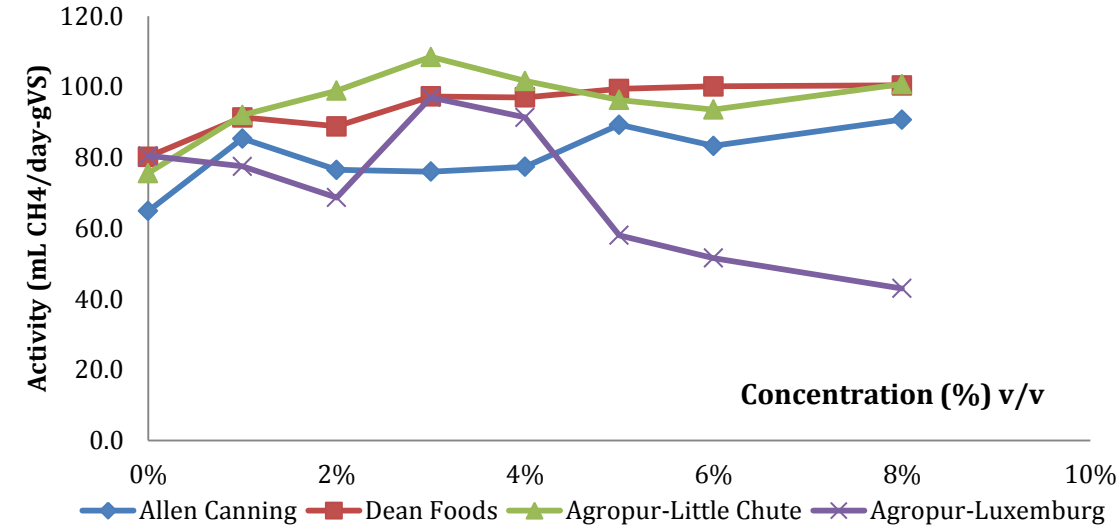


Figure 3.2: Theoretical and Observed BMP Results

3.1.3 Co-Digestate Anaerobic Toxicity Assay (ATA) Results

The ATA tests resulted in synergistic, neutral and antagonistic outcomes when the four co-digestates were digested separately with calcium acetate as the main non-limiting substrate (see Figure 3.3). The Vegetable Blancher Water, Milk Processing Wash Water and Cheese Production DAF Tank Sludge and Float all resulted in synergistic outcomes. The maximum CH_4 yield increased more than 35% for the Vegetable Blancher Water, 25% for the Milk Processing Wash Water and 40% for the Cheese Production DAF Tank Sludge and Float. The Cheese Production DAF Tank Sludge demonstrated mixed outcomes; first exhibiting antagonism, then synergism, and then antagonism (IC_{50}=4%).

The reason for mixed results is unknown and further research could be conducted to determine the variation.



n=3

Figure 3.3: Anaerobic Toxicity Assay of Co-Digestates

3.2 Performance of Bench-Scale Anaerobic Digesters

The performance of the bench-scale anaerobic co-digestion process is described in the following sections.

3.2.1 Digester Performance Results for Phases 1-4

The analytical results from Phase 1 to 4 varied for the bench-scale anaerobic digesters (see Tables 3.3-3.6). The original scope of the project did not include Phases 3 and 4; therefore, more analytical results are presented for Phases 1 and 2. Phases 3 and 4 were added during the study in an attempt to determine the maximum OLR for each digester set. The analytical tests conducted during Phases 3 and 4 were done to focus on

the effect of high organic loading rates and lower solids retention times on CH_4 production, VSR, and digester VFA concentrations.

Table 3.3: Phase 1 Steady-State Analytical Results

	Digester Set A		Digester Set B		Digester Set C		Feed	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
VSR, %	42	8.9	41	9.3	48	4.4		
Methane, %	66.9*	4.1	68.7	0.9	69.2	1.7		
pH	7.17	6.90-7.30	7.2	7.09-7.32	7.22	7.10-7.35	5.86	5.54-6.37
TS, g/L	29.8	4.2	30.7	4.1	27.2*	1.1	45.1	2.4
VS, g/L	20.6	2.8	20.8	2.8	18.3*	0.8	35.4	1.6
COD, g/L	31.3	5.9	33.4	5.1	30.9*	1.9	58.8	3.8
sCOD, g/L	0.79*	0.22	0.59	0.025	0.6	0.041	2.9	0.36
Alkalinity, mg/L as $CaCO_3$	3500	320	3800	150	4000	120		
Biogas Production, L/L-day	1.51	0.19	1.09	0.16	0.94	0.11		
VFAs, mg/L**	<50	--	<50	--	<50	--	2900	600

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table 3.4: Phase 2 Steady-State Analytical Results

	Digester Set A		Digester Set B		Digester Set C		Feed+Codigestate	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
VSR, %	45	5.4	47	6.5	50	5.6		
Methane, %	68.6	1.3	69.3	1.6	70.2	1.5		
pH	7.05	6.81-7.21	7.00	6.82-7.12	7.04	6.93-7.21		
TS, g/L	26.5*	1.4	26.4*	1.9	25.7	2.2	42.4	2.4
VS, g/L	18.6	1.1	18.2	1.6	17.6	1.9	34.5	1.9
COD, g/L	32.5	1.3	29.7	5.5	30.3	3.0	57.3	3.7
sCOD, g/L	0.45	0.03	0.45	0.03	0.48	0.04	4.6	1.4
Alkalinity, mg/L as $CaCO_3$	3700	420	4100	290	4400	220		
Biogas Production, L/L-day	1.81	0.22	1.42	0.15	1.09	0.08		
VFAs, mg/L**	<50	--	<50	--	<50	--	3100	660

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table 3.5: Phase 3 Steady-State Analytical Results

	Digester Set A		Digester Set B		Digester Set C		Feed+Codigestate	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
VSR, %	51	9	53	13	53	4		
Methane, %	67.8	2.4	67.4	2.5	65.7*	1.6		
pH	6.85	6.70-7.04	6.83	6.72-6.97	6.84	6.77-6.98		
TS, g/L	21.6	2.8	20.5	3	21.7*	0.9	36.8	1.9
VS, g/L	14.7	2.1	13.7	2.1	14.3*	0.6	29.9	1.8
COD, g/L	29.1	1.9	24.9*	2.5	25.6*	1.0	50.4	4.3
sCOD, g/L	0.65*	0.08	0.44	0.04	0.46	0.03	3.8	0.73
Alkalinity, mg/L as $CaCO_3$	3000	240	3200	180	3100	50		
Biogas Production, L/L-day	1.99	0.12	1.62	0.14	1.35	0.16		
VFAs, mg/L**	<50	--	<50	--	<50	--	2800	670

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table 3.6: Phase 4 Analytical Results

	Digester Set A		Digester Set B		Digester Set C		Feed+Codigestate	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
VSR, %	42	10	43	5	52	6		
Methane, %	63.3	3.2	55.6	8	64.7	1.7		
pH	6.75	6.50-6.99	6.43	5.28-7.05	6.72	6.58-6.99		
TS, g/L	24.3	1.2	22.2	1.0	19.1	0.8		
VS, g/L	16.1	1.1	14.5	0.5	11.7	0.4		
Biogas Production, L/L-day	1.9	0.58	0.57	0.12	1.97	0.24		
VFAs, mg/L**	95	95	1300	790	<50	--	1800	470

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

3.3 CH_4 Production and Composition

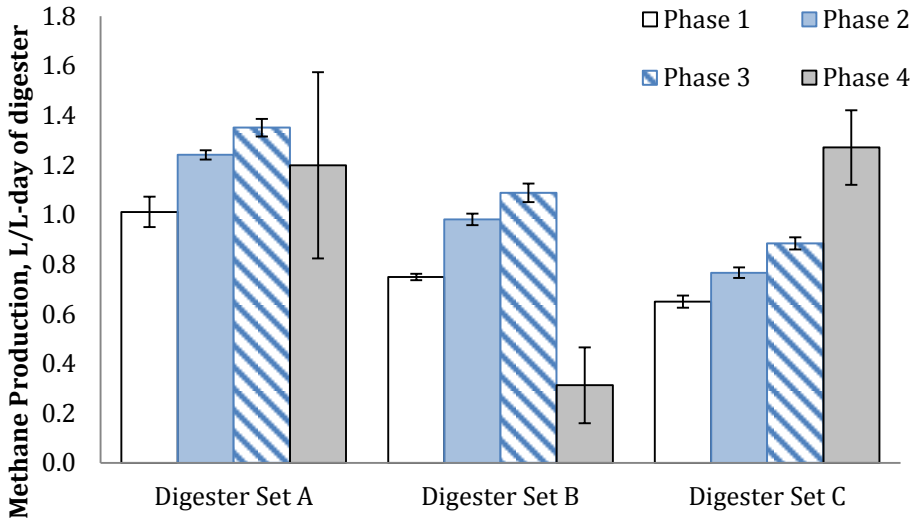
Production of CH_4 (L/day) increased from Phase 1 to Phase 3 during steady-state operation. During Phase 4 the only increase in CH_4 production was observed in Digester Set C, while Digester Sets A and B exhibited a decrease (see Figure 3.4). The CH_4 production rates for each set of digesters varied with the different organic loading rates. Digester Set A, Digester Set B and Digester Set C exhibited an average increase of 23%, 31% and 18% in CH_4 production from Phase 1 to Phase 2. The theoretical, expected CH_4 production increase calculated for Phase 1 to Phase 2 and the data are shown in Figure 3.5. The theoretical CH_4 production was calculated by determining the additional COD added from the co-digestate mixture and multiplying that by a conversion factor of 400 mL CH_4/g COD to find the theoretical maximum additional CH_4. The theoretical expected average increase in CH_4 production for Digester Set A, Digester Set B and Digester Set C was 27%, 23% and 21%, respectively (see Table 3.7). The observed and theoretical CH_4 production rates were not statistically different ($P>0.05$).

For all digester sets, CH_4 biogas concentrations increased during Phase 2, but decreased during Phases 3 and 4. The CH_4 concentrations during steady-state operation are presented in Figure 3.6. The increases in CH_4 concentrations from Phase 1 to Phase 2 were statistically significant ($P<0.05$) for each digester set. During Phase 3 the additional volume of co-digestate resulted in a decrease in CH_4 concentration that was statistically significant ($P<0.05$) when compared to Phase 2. In Phase 4, bench-scale digesters received the largest volume per day of co-digestate causing the biogas CH_4

concentrations to drop to the lowest values of the study. The difference in CH_4 concentrations measured in Phases 3 and 4 were statistically significant ($P<0.05$).

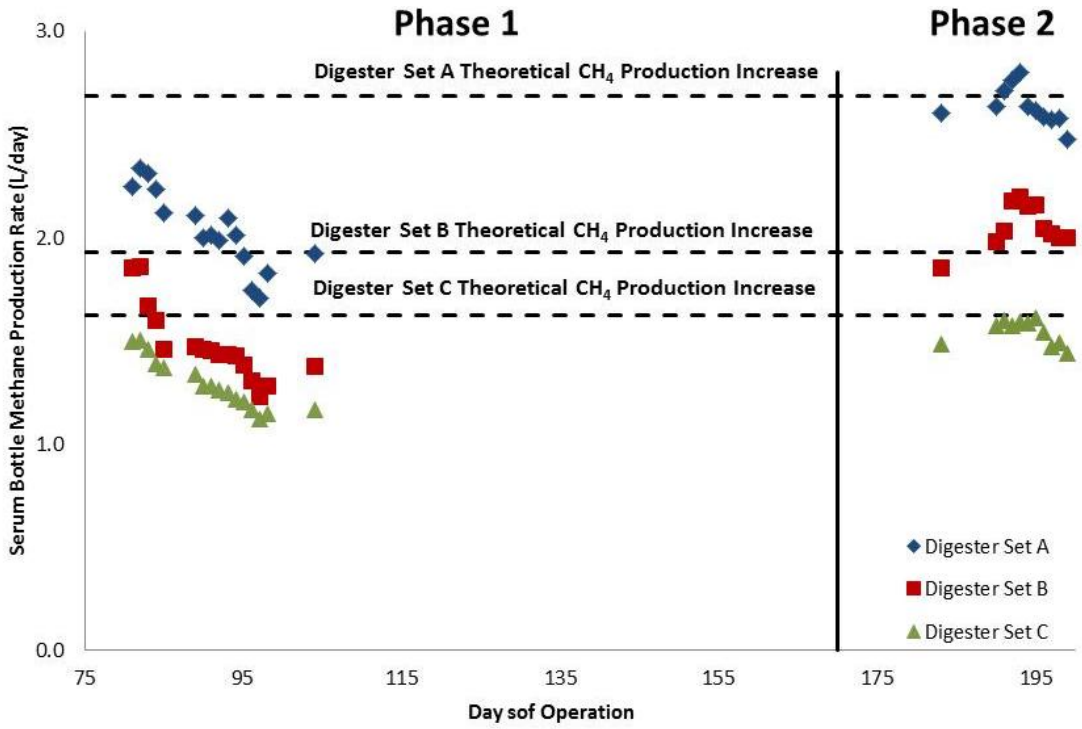
Typical biogas engine requirements stipulate a maximum siloxanes concentration in biogas of 10 mg/m^3 (Smith *et al.*, 2007). None of the biogas measurements exceeded 3 mg/m^3. No significant changes in siloxane concentrations were observed from Phase 1 to Phase 2 (see Figure 3.7). The average siloxane concentration in Digester set A decreased while the average siloxane concentrations increased in Digester Set B and Digester Set C, but the changes in the digester sets were not statistically significant ($P>0.05$).

The H_2S concentrations during steady-state in Phase 1 and Phase 2 had mixed results (see Figure 3.8). The average H_2S concentrations from Digester Set A increased from Phase 1 to Phase 2 and was statistically significant ($P<0.05$). The changes for Digester Set B and Digester Set C were not statistically significant ($P>0.05$). For engines and other equipment, H_2S concentration should not exceed 3,000 ppmv (Smith *et al.*, 2007). The measured concentration did exceed this maximum value. Ferric chloride can be added to the full-scale digesters to decrease the final H_2S concentrations.



Phase 1 n=18, Phase 2 n=17, Phase 3 n=5, Phase 4 n=2
error bars = standard deviation

Figure 3.4: Steady-State CH_4 Production Results

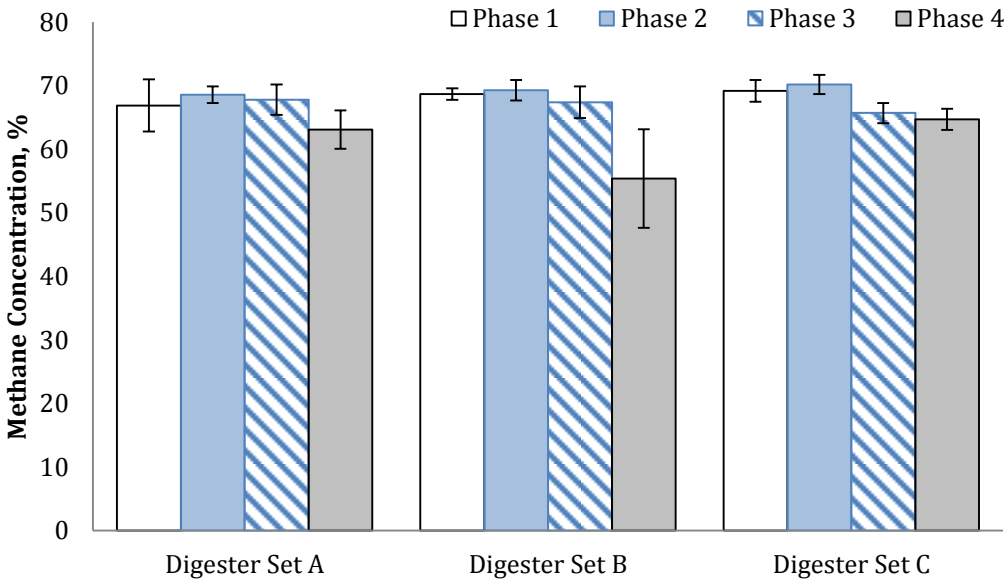


n=31

Figure 3.5: Theoretical CH_4 Production during Phase 2

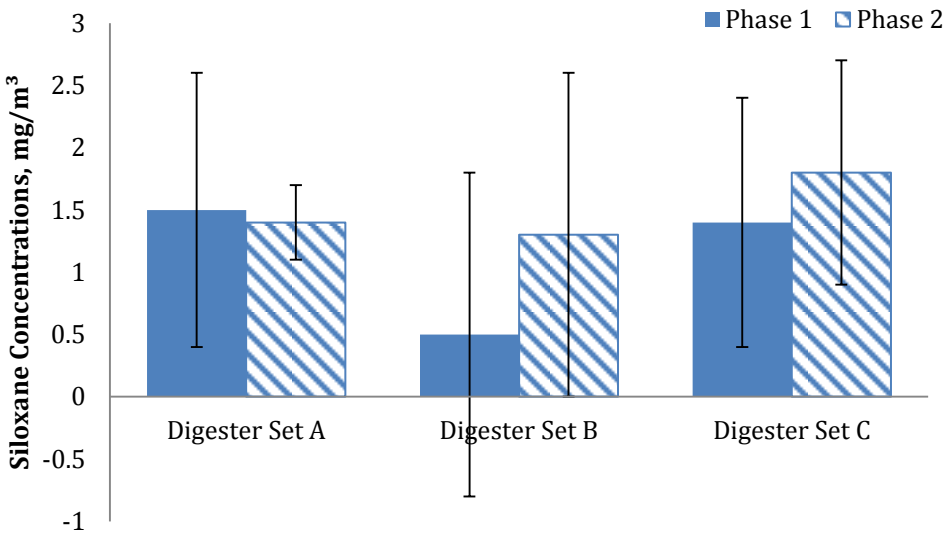
Table 3.7: Phase 1 and Phase 2 Theoretical Biogas Production Increase

	Digester Set A		Digester Set B		Digester Set C	
	Average	Stdev	Average	Stdev	Average	Stdev
Phase 1 CH_4 production (L/day)	2.02	0.25	1.5	0.22	1.3	0.15
Phase 2 CH_4 production (L/day)	2.48	0.30	1.96	0.20	1.53	0.11
Theoretical CH_4 from co-digestates (L/day)	0.73	0.12	0.45	0.09	0.34	0.07
Theoretical CH_4 Production (L/day)	2.75	0.28	1.95	0.24	1.64	0.17
Theoretical increase %	26.5%		23.1%		20.7%	
Observed increase in CH_4 from co-digestates	23.0%		31.0%		18.0%	
Difference in Observed vs. Theoretical	-3.5%		7.9%		-2.7%	



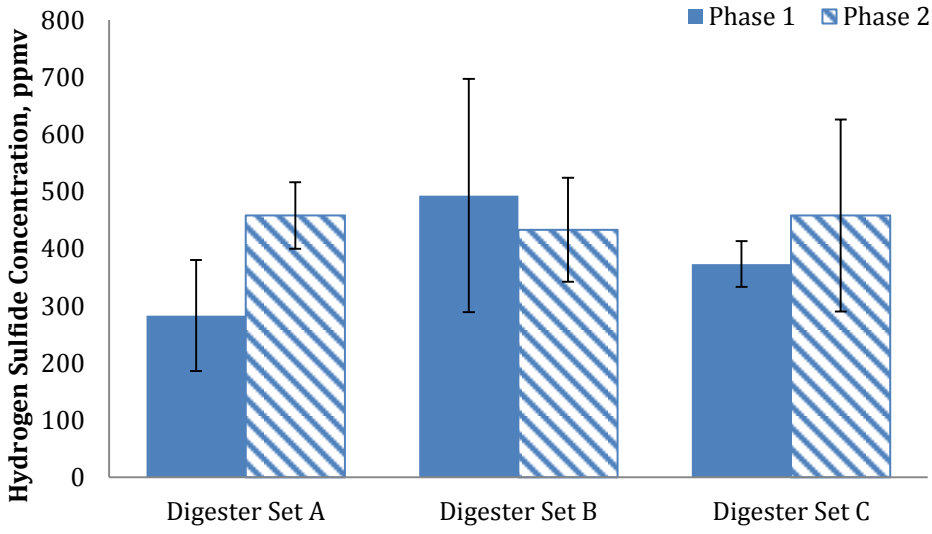
Phase 1 n=62, Phase 2 n=58, Phase 3 n=42, Phase 4 n=24
error bars = standard deviation

Figure 3.6: Steady-State CH_4 Concentrations



Phase 1 n=6, Phase 2 n=6
error bars = standard deviation

Figure 3.7: Steady-State Siloxane Concentrations



Phase 1 n=6, Phase 2 n=6
error bars = standard deviation

Figure 3.8: Steady-State H_2S Concentrations

3.4 Digested Sludge Dewaterability

Co-digestion had no significant impact on dewaterability or polymer dose required to achieve maximum cake solids. Multiple samples of digested sludge were sent to various dewatering vendors to test different polymers and dewatering techniques. The techniques used, polymer dose and maximum achievable cake solids data are presented in Figure 3.9. The complete sets of data tables are presented in the Appendix (A22-A23).

There was no statistically significant (P>0.05) difference between cake solids concentrations from Phase 1 to Phase 2. The polymer dose range for Phase 1 was approximately 22 to 28 lb/ dry ton and the range for Phase 2 was approximately 17 to 27 lb/dry ton. Though the average polymer dose was slightly lower during Phase 2, the difference in overall dose required was not statistically significant (P>0.05).

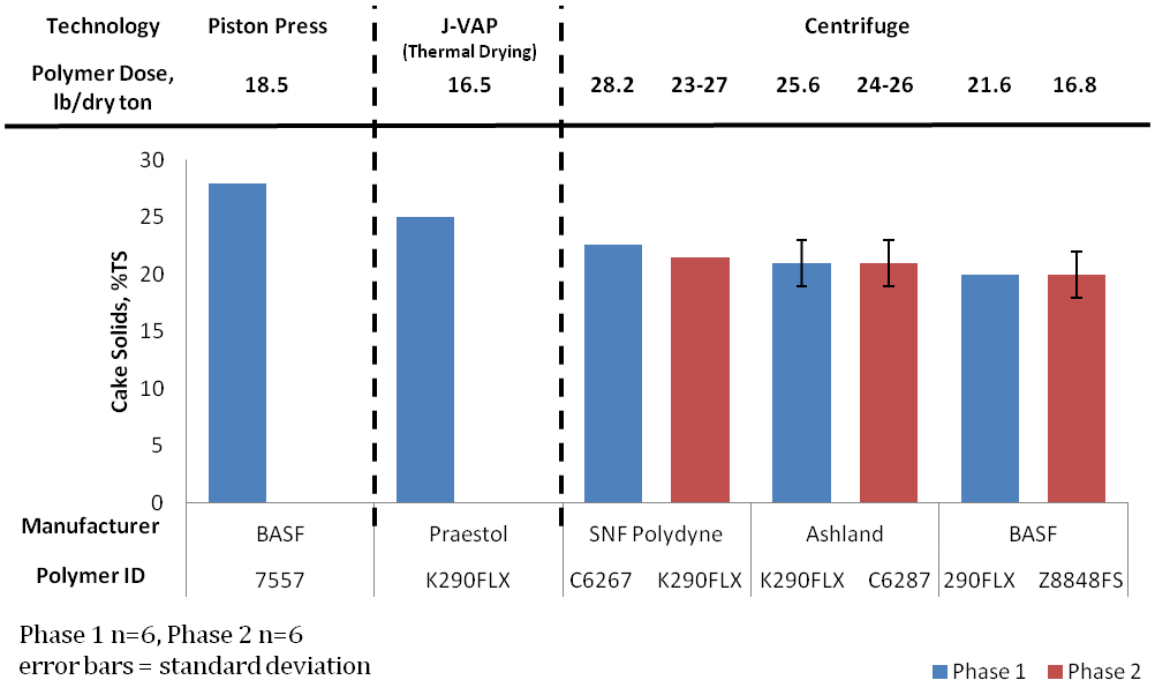


Figure 3.9: Cake Solids and Polymer Dose

3.5 Bench-Scale Anaerobic Co-Digestion Operation

The operation and performance of the bench-scale anaerobic co-digesters is discussed below.

3.5.1 Increased Organic Loading with Co-Digestion

During the four phases of operation, the OLR of each digester set was increased. The increase in OLR was a result of the additional volume of co-digestate added during Phases 2, 3 and 4. Because the volume of municipal sludge fed and the digester volumes were kept constant throughout the duration of the study, the HRT and SRT values decreased as volume of co-digestates and OLR were increased. The OLR significantly increased from Phase 1 to Phase 4 (see Figure 3.10). The SRT for each digester set decreased during each phase of operation (see Figure 3.11). Despite the increase in OLR and decrease in SRT, the bench-scale anaerobic digesters were still able to operate under most conditions.

The bench-scale anaerobic digesters consistently demonstrated good operation during Phases 1 through 3; it was not until reaching quasi-steady-state during Phase 4 that some of the digesters went sour or failed. The criteria used to express healthy operation included the following: average pH (>6.8) and VFA (<2,000 mg/L as acetic acid). The results for Phase 1 through Phase 4 operation are shown in Table 3.8.

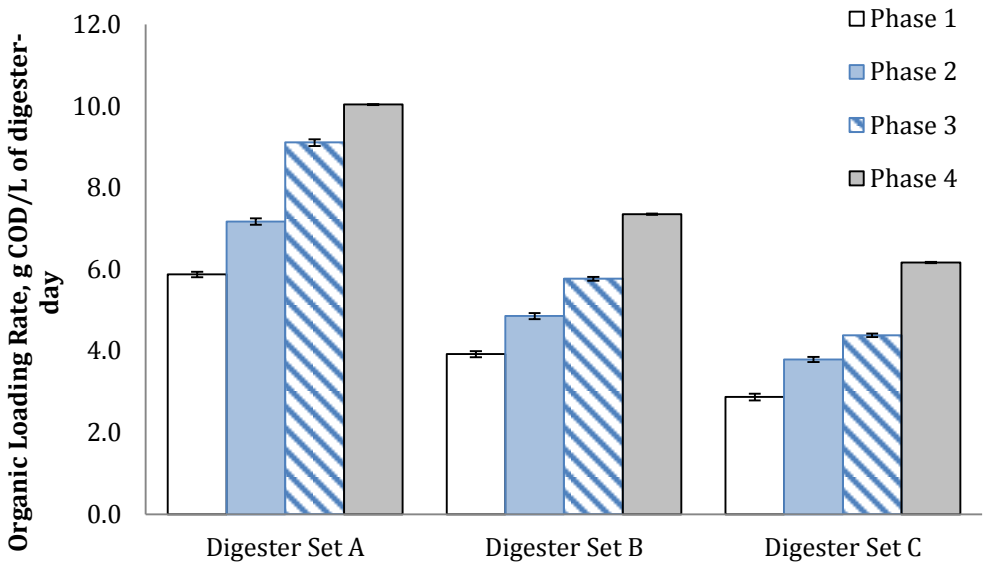
The high volume of co-digestate mix added in Phase 4 caused all three sets of digesters to decrease in operational health. Upon reaching quasi-steady-state, all three digester sets were functioning at stressed levels, and eventually Digester Set B failed (pH

decreased below 6.5, the CH_4 concentration decreased below 60% and total VFA concentration increased above 2,000 mg/L as acetic acid). The effect of organic loading rate on the healthy operation factors can be seen in Figures 3.12 and 3.13.

The volumetric ratio of municipal sludge:co-digestates appeared to be the reason why the bench-scale digesters were able to operate at higher OLRs than typically seen in CSTRs. A completely mixed anaerobic digester has the ability to run at a minimum of a 4-day SRT (Metcalf and Eddy, 2003). A typical loading rate for a CSTR at a 15- to 20-day SRT digesting municipal wastewater sludge is 2.4 to 6.8 g COD/L-day (Metcalf and Eddy, 2003). Surprisingly, the bench-scale digesters fed a mixture of co-digestate and municipal sludge were able to function at higher OLR and lower SRT than the values described above (see Figures 3.10 and 3.11). The co-digestate mixture was ostensibly comprised of a high fraction of readily degradable substrates, such as acetic acid, while the municipal wastewater sludge was composed of more slowly degradable substrates, such as cellulose, that take longer to break down before being converted to CH_4. In addition, primary sludge contains a mixture of microorganisms, including methanogens that carry out methanogenesis. Therefore, by adding TPS, beneficial microorganisms were ostensibly continuously added to the digesters. The blends of readily available and slower digesting wastes as well as the continuous addition of beneficial microorganisms are possible explanations as to why such high, sustainable OLRs were achieved when digester feed with a high municipal sludge:co-digestate volumetric ratio was used.

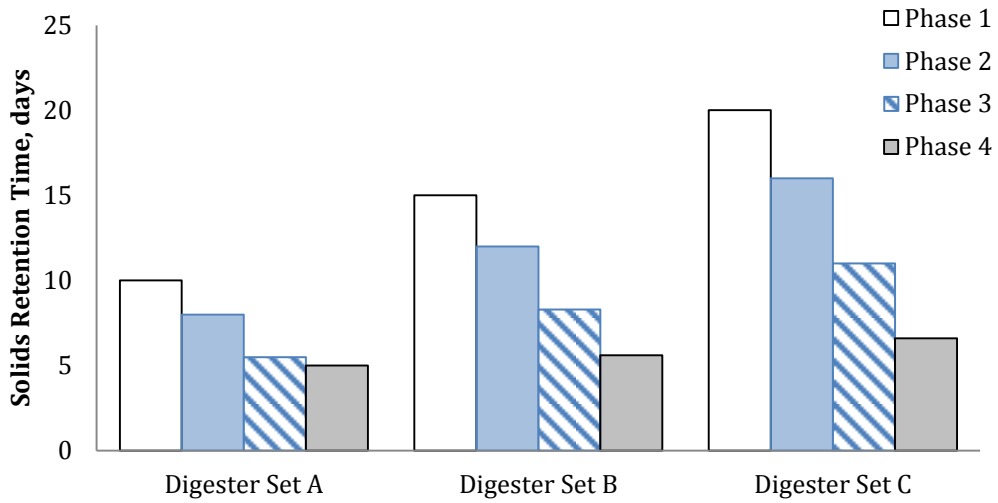
Others have operated lab-scale digesters that were fed a mixture of synthetic industrial wastewater (non-fat dry milk and nutrients) (Venkiteshwaran, 2013). The synthetic wastewater was highly degradable much like the co-digestates used in this co-

digestion study. Because the synthetic wastewater was highly degradable, it acidified quickly resulting in high VFA concentration. The measured total VFA concentrations ranged from 0.4 to 7 g/L as acetic acid in the digesters when the digesters were only fed at an OLR of 3 g COD/L-day. When the OLR was increased above 3 g COD/L-day, the VFA concentrations increase to levels that cause digester failure. This failure may have been avoided if municipal wastewater sludge was added in addition to the synthetic wastewater.



Phase 1 n=238, Phase 2 n=182, Phase 3 n=86, Phase 4 n=38
error bars = standard deviation

Figure 3.10: Organic Loading Rates of Bench-Scale Digesters



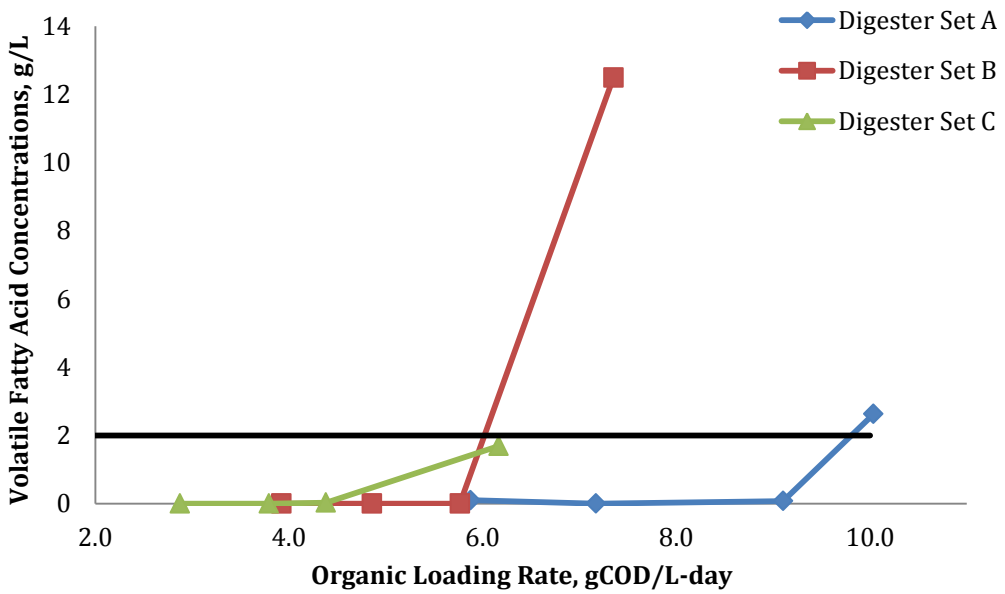
Phase 1 n=238, Phase 2 n=182, Phase 3 n=86, Phase 4 n=38

Figure 3.11: Solids Retention Times for Bench-Scale Digesters

Table 3.8: Digester Operational Health Results

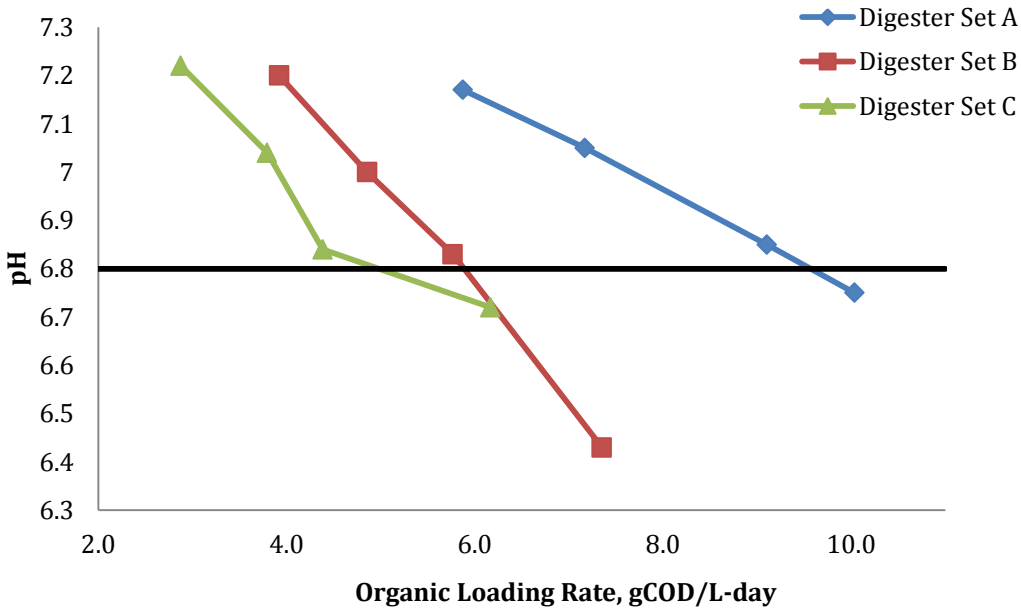
High OLR Healthy Operation Criteria								
	pH		Biogas Production, L/L		CH_4 %		VFA, Acetic Acid (mg/L)	
	Average	Stdev	Average	Stdev	Average	Stdev	Average	Stdev
Phase 1								
Digester Set A	7.17	6.90-7.30	1.51	0.19	66.9*	4.1	<50	--
Digester Set B	7.2	7.09-7.32	1.09	0.16	68.7	0.9	<50	--
Digester Set C	7.22	7.10-7.35	0.94	0.11	69.2	1.7	<50	--
Phase 2								
Digester Set A	7.05	6.81-7.21	1.81	0.22	68.6	1.3	<50	--
Digester Set B	7.00	6.82-7.12	1.42	0.15	69.3	1.6	<50	--
Digester Set C	7.04	6.93-7.21	1.09	0.08	70.2	1.5	<50	--
Phase 3								
Digester Set A	6.85	6.70-7.04	1.99	0.12	67.8	2.4	<50	--
Digester Set B	6.83	6.72-6.97	1.62	0.14	67.4	2.5	<50	--
Digester Set C	6.84	6.77-6.98	1.35	0.16	65.7*	1.6	<50	--
Phase 4								
Digester Set A	6.75	6.50-6.99	1.9*	0.58	63.3	3.2	2,500	2,200
Digester Set B	6.43	5.28-7.05	0.57	0.12	55.6	8	12,340	2,000
Digester Set C	6.72	6.58-6.99	1.97*	0.24	64.7	1.7	1,700	1,200

*Duplicate digesters were statistically different



Phase 1 n=30, Phase 2 n=30, Phase 3 n=30, Phase 4 n=30

Figure 3.12: Volatile Fatty Acids versus OLR



Phase 1 n=30, Phase 2 n=30, Phase 3 n=30, Phase 4 n=30

Figure 3.13: pH versus OLR

3.5.2 Increased VSR with Co-Digestion

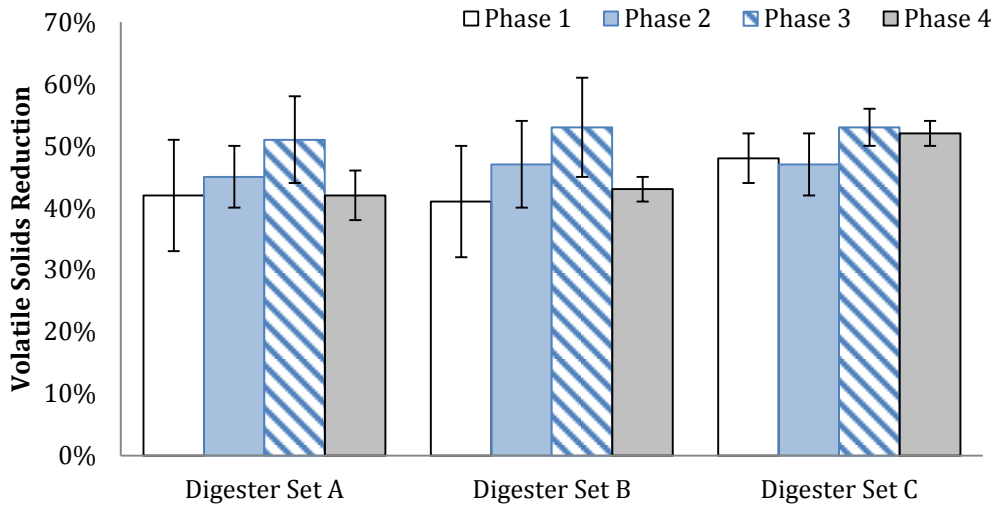
An increase in VSR was observed from Phase 1 to Phase 3, but a decrease was observed during Phase 4 (see Figure 3.14). The addition of co-digestates often allows for higher VSR to be achieved due to the addition of highly degradable waste. The VSR for all four phases can be seen in Table 3.9. The average VSR increased from Phase 1 to Phase 2 and was statistically significant ($P<0.05$) for Digester Set A and Digester Set B, but was not statistically significant ($P>0.05$) for Digester Set C.

During Phase 3 the additional volume of co-digestate added to the bench-scale digesters resulted in an increase in VSR. The increased VSR from Phase 2 to Phase 3 was statistically significant ($P<0.05$) for all three sets of digesters. During Phase 4, the bench-scale digesters received the largest volume of co-digestate to run the digesters at the maximum loading. At the highest loading, the digesters operated at lower efficiency. The VSR decreased for all three sets of digesters from Phase 3 to Phase 4. The decrease in VSR for Digester Set A and Digester Set B was statistically significant ($P<0.05$), while the decrease in VSR for Digester Set C was not statistically significant ($P>0.05$).

The addition of co-digestate during Phase 2 and Phase 3 proved to be beneficial in increasing the VSR. The increased loading during Phase 4 was so high that digester health decreased, causing failure in all digester sets.

Table 3.9: Volatile Solids Reduction of Bench-Scale Digesters

	Phase 1		Phase 2		Phase 3		Phase 4	
	Average	Stdev	Average	Stdev	Average	Stdev	Average	Stdev
Digester Set A	42%	9%	45%	5%	51%	7%	42%	4%
Digester Set B	41%	9%	47%	7%	53%	8%	43%	2%
Digester Set C	48%	4%	47%	5%	53%	3%	52%	2%



Phase 1 n=56, Phase 2 n=60, Phase 3 n=48, Phase 4 n=30
error bars = standard deviation

Figure 3.14: Volatile Solids Reduction for Bench-Scale Digesters

3.5.3 Increased CH_4 Production with Co-Digestion

Co-digestion resulted in increased CH_4 production for Phase 2 and Phase 3, but mixed results in Phase 4 (see Figure 3.4). The co-digestates added to the bench-scale anaerobic digesters were predicted by BMP testing to increase CH_4 production, because the co-digestates can easily be utilized and converted into CH_4. The CH_4 production values for each phase can be seen in Table 3.10.

Phase 2 co-digestion demonstrated an increase in CH_4 production over Phase 1. The increase in CH_4 production was statistically significant ($P<0.05$). The increase in CH_4 production was due to the addition of the co-digestates added. During Phase 3 the CH_4 production increased, but was not statistically significant ($P>0.05$) for Digester Set A and Digester Set B, however, the CH_4 production increase was statistically significant ($P<0.05$) for Digester Set C. During Phase 4, the largest volume of co-digestate was added to achieve the maximum OLR. The maximum OLR resulted in a decrease in CH_4 production for Digester Set A and Digester Set B, while Digester Set C saw a dramatic increase in CH_4 production. The change in CH_4 production for each digester set was statistically significant ($P<0.05$).

The volume of co-digestate added during Phase 2 and Phase 3 lead to an increase in CH_4 production, because the co-digestates were highly degradable. During Phase 4, the digesters received the largest volume of co-digestate, causing some of the digesters to operate under stressed conditions. The stressed conditions ultimately lead to lower CH_4 production in Digester Set A and Digester Set B. Digester Set B was run until failure, resulting in the largest decrease in CH_4 production during digester operation.

Table 3.10: Steady-State CH_4 Production, L/L-day of digester

	Phase 1		Phase 2		Phase 3		Phase 4	
	Average	**STDEV**	**Average**	**STDEV**	**Average**	**STDEV**	**Average**	**STDEV**
Digester Set A	1.0	0.06	1.2	0.02	1.4	0.04	1.2	0.38
Digester Set B	0.7	0.01	1.0	0.02	1.1	0.04	0.3	0.15
Digester Set C	0.6	0.02	0.8	0.02	0.9	0.02	1.3	0.15

3.5.4 Synergistic Results from Co-digestion

The effect of co-digestion is often unknown until bench-scale studies are conducted. Prior to bench-scale operation, a BMP was run to determine the potential outcomes of digesting different co-digestates.

Comparing the theoretical and observed BMP results, it was determined that the Milk Processing Wash Water resulted in a synergistic outcome, and the three co-digestates and the co-digestate mixture resulted in a neutral outcome. From the results it appears that co-digestion will result in a neutral outcome in terms of CH_4 yield when the co-digestates are digested with municipal sludges. No antagonistic outcomes were observed during BMP testing.

All CH_4 production results were also considered to determine what outcomes were observed in the bench-scale study. The CH_4 production results stated in section 3.4.3 demonstrated that adding co-digestates was statistically significant for all three digesters in Phase 2, Digester Set A and Digester Set B in Phase 3 and Digester Set A and Digester Set B in Phase 4. CH_4 production varied for each phase due to the volumes of co-digestates added.

3.5.5 Co-Digestate OLR and Sustainable Digester Health

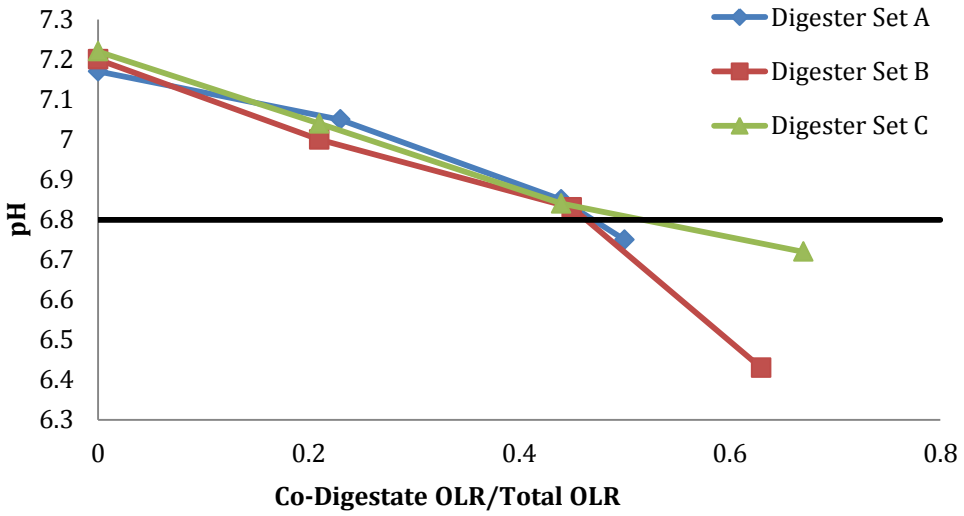
Municipal sludges consist of a high fraction of constituents such as cellulose which is slowly fermentable; therefore, it does not acidify extremely rapidly. TPS also contains a significant amount of microorganisms that, when added to anaerobic digesters,

can have beneficial effects. The co-digestates added during Phases 2, 3 and 4 consisted of constituents which can easily be degraded/acidified and utilized in the anaerobic digestion process. Because the municipal sludges take longer to break down and be utilized, the readily degradable constituents from the co-digestates could be broken down and utilized more rapidly than the municipal sludge. This combination of fast and slow degrading wastes allows acids to be used throughout the anaerobic digestion process rather than all of the wastes being acidified at once and causing digesters to go sour.

The ratio of co-digestate OLR to the total OLR is important because having a certain ratio can allow anaerobic digesters to run at lower SRTs and higher OLRs than attainable when co-digestates are treated alone. The ratio of co-digestate OLR to the total OLR versus digester parameters is shown in Figures 3.15-3.17. Once the ratio increased to a value higher than 0.45 under the conditions studied, the digesters failed.

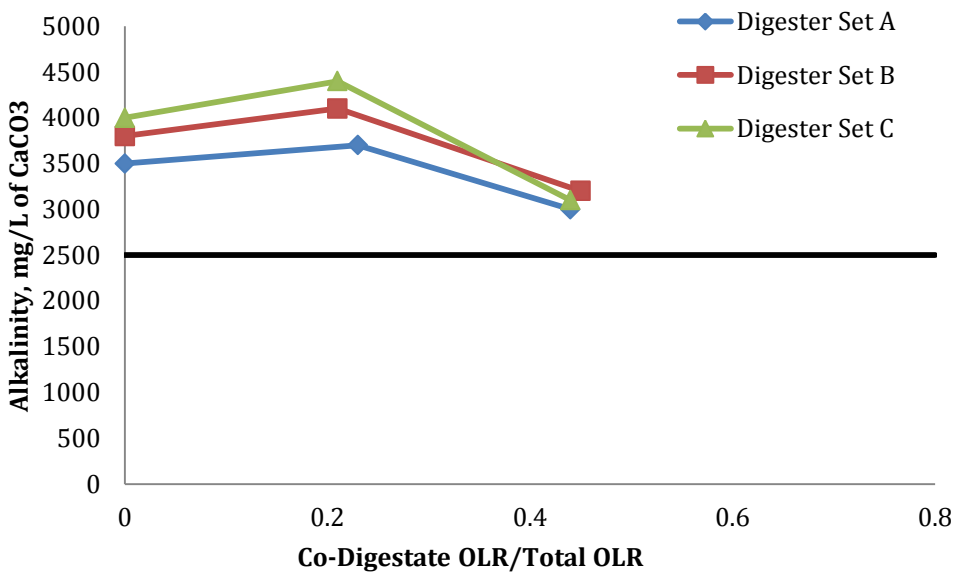
During Phases 2, 3 and 4, the ratio of co-digestate OLR to the total OLR increased significantly from 0 co-digestate OLR/total OLR during Phase 1 up to 0.67 co-digestate OLR/total OLR during Phase 4. This increase degraded the digester health. In Figure 3.15 as the ratio increased, the pH decreased until the values were below the acceptable limits for healthy operation. The pH dropped so low for Digester Set B that the set finally failed at the end of the study. Though no alkalinity data were taken during Phase 4, Figure 3.16 shows that the alkalinity dropped significantly from Phase 2 to Phase 3, approaching the acceptable lower limit of healthy operation. The increase in the co-digestate OLR ratio produced no detectable VFAs until Phase 4 when the ratio increased above 0.45 co-digestate OLR/total OLR for all sets of digesters. This increase caused large increases in VFA concentrations in all digester sets, two of which surpassed

the acceptable limit for healthy operation. The increase in Digester Set B was so significant that the digester ultimately failed and all operation ceased.



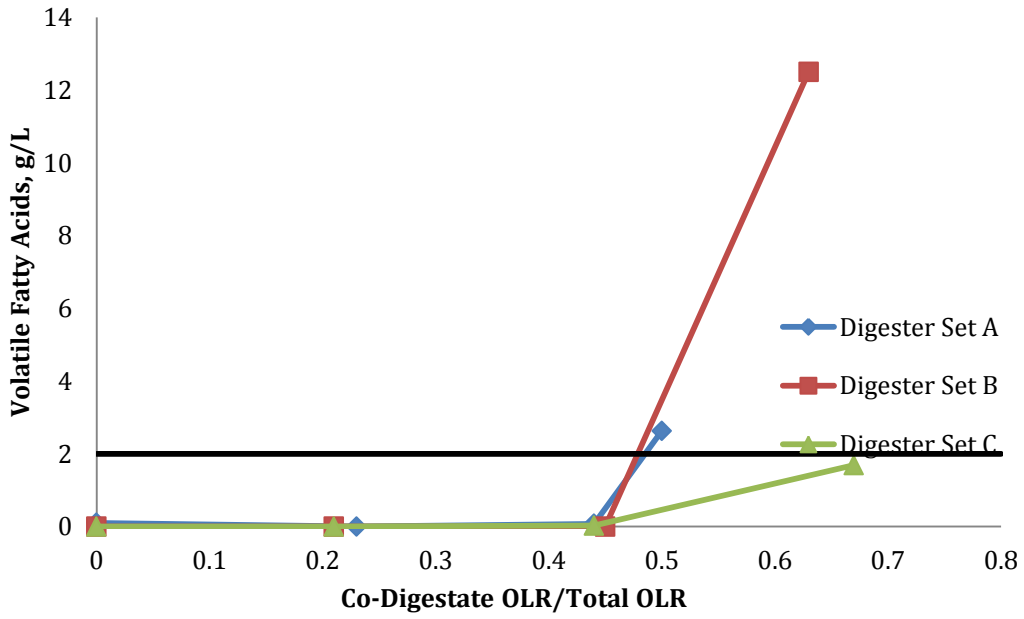
Phase 1 n=238, Phase 2 n=182, Phase 3 n=86, Phase 4 n=38

Figure 3.15: pH versus Co-Digestate OLR/Total OLR



Phase 1 n=20, Phase 2 n=19, Phase 3 n=14

Figure 3.16: Alkalinity versus Co-Digestate OLR/Total OLR



Phase 1 n=30, Phase 2 n=30, Phase 3 n=30, Phase 4 n=30

Figure 3.17: VFAs versus Co-Digestate OLR/Total OLR

4 Conclusions

Anaerobic digesters are sensitive to high OLRs. When OLRs are too high digesters can often become stressed and fail. Co-digestion has been proven to be beneficial when the co-digestates are added in adequate amounts, but large amounts can be toxic; therefore, the volumes of co-digestates added needs to be carefully monitored. During Phase 3 and Phase 4, higher volumes of co-digestate mix were added to the bench-scale digesters to determine how the volumes of municipal sludge and co-digestates affect digester operation. As hypothesized, wastewater sludge and high-strength waste complimented each other allowing high OLRs to be reached at low solids retention times. The volumes of co-digestate added during Phase 4 did cause the VFA concentrations to increase as well as lowering the pH.

Studies have shown that co-digestion can increase VSR in anaerobic digesters. Co-digestates are often highly degradable compounds that when added to anaerobic digesters allows the VSR to increase. Phase 2 co-digestion demonstrated an average overall increase in VSR as hypothesized. The VSR increased during Phase 3, but decreased during Phase 4. Co-digestion has the potential to increase VSR; however, to ensure VSR does not decrease, the volume of co-digestates added needs to be carefully controlled to ensure the maximum amount of each waste will be degraded.

Co-digestates are often in the liquid form and consist mostly of readily degradable constituents which are quickly consumed by microorganisms and converted to biogas. The extra carbon added from co-digestates can often increase biogas production as well as CH_4 production. During Phase 2 and Phase 3 with the addition of co-digestates, higher

CH_4 production values were achieved as hypothesized. However, during Phase 4, because the digesters were fed such high volumes of co-digestates, mixed CH_4 production values were observed. Some of the duplicate digesters had increases in CH_4 production while others saw significant decreases in CH_4 production. Running anaerobic digesters at lower than 5 day SRTs and greater than 9 g/L of digester is not recommended.

High strength industrial wastes can contain different toxins or high metal concentrations that can be inhibitory when added to anaerobic digesters. Prior to running the bench-scale anaerobic digesters, two sets of BMP tests were conducted to determine if any synergistic, neutral or antagonistic outcomes could be expected. The Milk Processing Wash Water proved to have a synergistic effect when digested with municipal sludge, while the other three co-digestates and co-digestate mix resulted in neutral outcomes, opposite of what was hypothesized. Although the BMPs did not all result in synergistic outcomes, the combination of co-digestates when digested with municipal sludge and fed to the bench-scale digesters did prove to have beneficial outcomes during the three phases of co-digestion.

During each phase of co-digestion, the ratio of co-digestate OLR to the total OLR increased until reaching its maximum during Phase 4. A ratio of <0.45 co-digestate OLR/total OLR was beneficial for operating the anaerobic digesters under the conditions studied, but when the ratio was >0.45 co-digestate OLR/total OLR the bench-scale anaerobic digesters were stressed or sour. Phase 4 was run at the highest OLRs, which is also a cause of digester failure, but the ratio of co-digestate OLR to total OLR is believed to be the root cause of failure, however; the ratio needs to be investigated further.

Though some digesters failed in Phase 4, Phase 3 proved that the bench-scale digesters could still be operated successfully at higher than normal OLRs and lower than normal SRTs due to the fact that a large volume of the feed consisted of the municipal sludge.

Co-digestion of four high strength industrial wastes was successful in lab-scale. The combination of industrial waste and municipal sludges proved to be the major factor to the successful operation of anaerobic bench-scale digesters at low SRTs and high OLRs.

5 References

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Appendix

Table A1: Comprehensive Industrial Waste Survey Results

Co-digestate description	Average COD (mg/L)	Daily Production Amount	Daily Production Unit	Average %TS	Average %VS	Haul Distance to GBMSD	pH	Average NH_3-N	Average TKN	Average TP*
Filter cake solids	2,000,000	--	--	10	8.1	6.5	N/A	140	46,000	9,600
High acid solids	1,400,000	--	--	9.9	9.1	6.5	N/A	780	31,000	4,200
Anaerobic contact WAS	240,000	9.3	wet tons	19	15	4.7	N/A	4,900	71,000	10,000
Paunch manure	240,000	33	wet tons	29	26	4.7	N/A	450	11,000	3,100
Primary wastewater sludge	160,000	--	--	11	9.4	6.5	5.9	11,000	50,000	3,200
Beer	110,000	64	gal	3.0	2.2	0.4	6.8	380	25,000	4,700
Cheese Production DAF Tank Sludge	110,000	5,500	gal	10	8.0	21	3.9	630	14,000	4,600
Somat Sludge	90,000	--	--	7.6	6.7	6.5	N/A	8,400	130,000	11,000
Vegetable Blancher Water	66,000	5,000	gal	5.7	4.8	19	6.6	400	13,000	3,700
Cheese Production DAF Tank Sludge and Float	38,000	11,000	gal	2.8	2.2	25	6.2	1,100	43,000	14,000
Pepper/pickle solids	38,000	--	--	5.8	3.4	2.8	4.1	1,200	23,000	2,700
Milk processing sour cream: Sample 2	30,000	13,000	gal	1.1	0.78	8.7	12	TBD	TBD	TBD
Milk Processing Wash Water	26,000	13,000	gal	1.2	0.94	8.7	12	TBD	TBD	TBD
Irrigation field corn	21,000	5,000	gal	0.98	0.83	19	4.5	700	82,000	7,900
Wastewater hole	15,000	8,500	gal	12	1	27	6.8	3,200	22,000	8,500
Cheese Wash Water	7,900	100,000	gal	0.69	0.52	10	9.7	4,000	19,000	8,100
Holding cell	7,400	8,500	gal	0.60	0.32	27	6.1	13,000	45,000	14,000
Cheese water (high chlorides)	6,800	19,000	gal	2.4	0.33	10	5.8	TBD	TBD	TBD
Primary wastewater water	5,700	--	--	2.3	0.26	6.5	6.7	29,000	42,000	1,300
Ridge and furrow	1,800	8,500	gal	0.37	0.13	27	7.9	7,700	ND	18,000

*TP is Total Phosphorus

Table A2: Five Industrial Wastes Chosen

	1		2		3		4		5	
	Vegetable Blancher Water		Milk Processing Wash Water		Cheese Production DAF Tank Sludge and Float		Cheese Production DAF Tank Sludge		Beer Waste	
Parameters	**Average**	**STDEV**	**Average**	**STDEV**	**Average**	**STDEV**	**Average**	**STDEV**	**Average**	**STDEV**
pH	6.2	0.34	9.3	1.1	6.3	0.42	4.4	0.2	6.8	--
TS (%)	26	16	1.5	0.29	29	17	47	27	1.4	0.2
VS (%)	17	10	1.3	0.32	23	15	32	24	1.4	0.2
Percent VS (%)	65.0	65	87	--	78	--	67	--	94.0	--
TSS (mg/L)	4.6	6.2	5.4	3.4	25	15	14	13	0.1	0.03
VSS (mg/L)	2.6	3	4.4	2.8	22	14	13	12	0.1	0.03
COD (mg/L)	23,000	13,000	27,000	6,300	27,000	12,000	60,000	38,000	84,000	1,600
sCOD (mg/L)	18,000	9,500	8,800	1,400	1,500	1,300	20,000	15,000	80,000	1,200
Total Phosphorus (mg/L)	160	--	51	--	350	--	310	--	72	--
NH_3-N (mg/L)	100	--	8	--	59	--	20	--	60	--
TKN (mg/L)	770	--	750	--	3,100	--	1,300	--	360	--
Oil and Grease (mg/L)	9	--	1,400	--	12	--	96	--	11	--
Alkalinity (mg/L as $CaCO_3$)	810	--	1,100	--	900	--	160	--	0	--
BMP (ml CH_4/gCOD)	310	3.6	210	6.2	200	36	280	16	--	--
ATA	IC_{50}>8%	--	IC_{50}>8%	--	IC_{50}>8%	--	IC_{50}=4%	--	--	--
Beryllium (µg/L)	19	--	2	--	5	--	1	--	3	--
Sodium (µg/L)	61	--	620	--	1,600	--	6,400	--	99	--
Magnesium (µg/L)	300	--	24	--	33	--	88	--	53	--
Aluminum (µg/L)	17,000	--	14,000	--	110,000	--	23,000	--	16,000	--
Potassium (mg/L)	1,700	--	140	--	170	--	400	--	210	--
Calcium (mg/L)	120	--	140	--	380	--	800	--	63	--
Chromium (µg/L)	120	--	130	--	58	--	190	--	310	--
Mangenese (µg/L)	470	--	36	--	110	--	140	--	99	--
Iron (mg/L)	7	--	2	--	7	--	19	--	3	--
Cobalt (µg/L)	41	--	10	--	55	--	41	--	21	--
Nickel (µg/L)	530	--	58	--	38	--	73	--	140	--
Copper (µg/L)	730	--	430	--	560	--	900	--	1,200	--
Zinc (µg/L)	5,200	--	3,200	--	980	--	1,300	--	550	--
Arsenic (µg/L)	16	--	3	--	3	--	3	--	4	--
Selenium (µg/L)	34	--	70	--	11	--	10	--	18	--
Molybdenum (µg/L)	45	--	8	--	12	--	16	--	9	--
Silver (µg/L)	34	--	14	--	33	--	21	--	33	--
Cadmium (µg/L)	40	--	51	--	7	--	22	--	11	--
Mercury (µg/L)	93	--	15	--	21	--	34	--	17	--
Lead (µg/L)	200	--	240	--	220	--	240	--	140	--
Quantity (gal/day)	5,000	--	13,000	--	11,000	--	5,500	--	64	--
Distance (miles)	19	--	9	--	25	--	21	--	0	--

Table A3: Phase 1 Steady-State Nutrient and Biogas Quality Results

Tests	(1 A)		(2 A)		(1 B)		(2 B)		(1 C)		(2 C)	
	Average	Stdev	Average	Stdev	Average	Stdev	Average	Stdev	Average	Stdev	Average	Stdev
NH-N (mg/L)	813	23	821	46	878	16	1007	38	1033	29	1053	23
TKN (mg/L)	2113	242	1569	368	2691	247	2878	410	2975	567	2477	193
Total Phosphorus(mg/L)	735	30	671	42	789	39	784	79	756	28	728	1
Soluble Phosphorus (mg/L)	81	3	79	6	147	56	165	18	181	23	144	8
H_2S (mg/L)	283	26	283	93	495	146	492	143	350	32	396	25

Table A4: Phase 2 Steady-State Nutrient and Biogas Quality Results

Tests	(1 A)		(2 A)		(1 B)		(2 B)		(1 C)		(2 C)	
	Average	Stdev	Average	Stdev	Average	Stdev	Average	Stdev	Average	Stdev	Average	Stdev
NH-N (mg/L)	820	25	800	13	870	7.6	870	13	930	5.0	1000	12
TKN (mg/L)	2200	18	2200	8.7	2300	42	2200	13	2200	35	2400	38
Total Phosphorus(mg/L)	510	15	550	61	510	20	570	22	570	17	560	8.7
Organic Phosphorus (mg/L)	510	15	520	55	490	22	560	24	540	17	540	18
H_2S (mg/L)	520	29	400	50	420	29	450	87	450	130	470	100
NH (mg/L)	9.0	2.6	8.3	2.9	8.7	3.2	8.0	3.5	7.7	3.2	7.7	2.5
Chlorine (mg/L)	ND*	--	ND*	--	ND*	--	ND*	--	ND*	--	ND*	--

Table A5: Phase 1 Steady-State Metals Results

Metals	Primary		WAS		(1 A)		(2 A)		(1 B)		(2 B)		(1 C)		(2 C)	
	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
Beryllium (µg/L)	33	40.2	15	100	28	33	20	52	29	52	22	32	31	42	36	62
Sodium (µg/L)	610	4.7	580	5.2	800	6.3	840	5.7	930	6.5	960	6.7	1,000	4.1	1,100	11
Magnesium (µg/L)	800	4.3	910	5.0	780	5.9	820	6.0	860	7.1	920	6.3	890	4.1	930	11
Aluminum (µg/L)	2,700,000	3.9	730,000	5.0	2,300,000	6.1	2,300,000	5.4	1,800,000	6.8	2,400,000	13	1,700,000	3.7	1,800,000	11
Potassium (mg/L)	180	4.8	1,100	5.0	750	5.9	780	5.5	800	6.2	830	6.1	850	4.0	930	11
Calcium (mg/L)	2,200	4.2	1,200	5.8	1,500	6.3	1,600	6.0	1,800	6.4	1,900	6.9	1,800	4.0	2,000	11
Chromium (µg/L)	4,400	3.3	3,300	4.9	3,800	6.0	5,200	6.3	4,700	6.6	4,600	6.2	5,600	4.6	6,000	11
Mangenese (µg/L)	10,000	5.2	63,000	5.8	24,000	6.3	25,000	5.4	27,000	6.3	29,000	6.6	28,000	4.2	30,000	11
Iron (mg/L)	1,300	3.8	870	4.7	1,100	6.1	1,200	5.4	1,200	6.2	1,300	6.5	1,300	4.0	1,300	11
Cobalt (µg/L)	500	6.3	930	13	880	6.2	920	10	1,000	10	1,100	7.8	1,100	9.7	1,500	6.1
Nickel (µg/L)	14,000	5.1	24,000	9.6	27,000	5.4	27,000	10	24,000	10	25,000	7.1	30,000	10	28,000	7.0
Copper (µg/L)	130,000	4.9	170,000	10	190,000	5.5	180,000	11	210,000	10	210,000	6.8	240,000	11	210,000	6.8
Zinc (µg/L)	73,000	5.7	56,000	9.4	81,000	5.7	81,000	11	91,000	10	94,000	6.5	110,000	11	100,000	7.0
Arsenic (µg/L)	1,600	3.8	2,700	11	2,600	5.3	2,600	9.4	3,100	10	3,500	6.4	3,300	13	3,300	6.1
Selenium (µg/L)	<0.000	N/A	1,100	79	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A
Molybdenum (µg/L)	240	8.9	230	7.9	240	2.5	260	5.5	240	4.8	290	4.9	280	5.6	290	4.0
Silver (µg/L)	5,100	7.8	160	5.8	180	3.1	210	5.7	250	5.1	300	5.7	250	2.8	260	2.6
Cadmium (µg/L)	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A
Mercury (µg/L)	150	1.3	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A
Lead (µg/L)	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A	<0.000	N/A

Table A6: Phase 2 Steady-State Metals Results

Metals	(1 A)		(2 A)		(1 B)		(2 B)		(1 C)		(2 C)	
	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
Beryllium (µg/L)	2.5	85	2.9	36	2.9	94	2.1	119	3.0	84	1.3	186
Sodium (µg/L)	400	0.7	420	0.7	420	0.8	420	0.8	420	0.6	430	0.3
Magnesium (µg/L)	230	0.6	200	0.7	210	0.6	230	0.7	230	0.5	250	0.6
Aluminum (µg/L)	340,000	0.7	340,000	0.6	350,000	0.7	310,000	0.7	350,000	0.3	370,000	0.5
Potassium (mg/L)	370	0.3	400	0.7	370	0.5	370	0.8	430	0.4	420	0.6
Calcium (mg/L)	680	0.5	690	1.0	700	0.6	770	1.0	740	0.3	750	0.5
Chromium (µg/L)	2,500	0.6	2,600	0.8	2,400	0.9	2,100	0.4	2,500	0.7	3,100	0.6
Mangenese (µg/L)	7,200	0.3	6,900	0.5	7,500	0.6	8,400	0.6	7,000	0.5	7,800	0.2
Iron (mg/L)	260	0.6	260	0.4	260	0.4	210	0.6	290	0.5	310	0.3
Cobalt (µg/L)	2,800	1.0	1,900	0.7	3,200	0.7	3,200	0.3	4,600	0.7	3,600	0.4
Nickel (µg/L)	5,100	1.3	4,600	0.4	5,200	0.6	5,600	0.5	6,500	0.6	4,600	0.6
Copper (µg/L)	11,000	1.2	11,000	0.8	11,000	0.6	12,000	0.5	11,000	0.7	16,000	0.5
Zinc (µg/L)	8,400	0.8	8,300	0.7	8,800	0.7	10,000	0.5	8,900	0.8	10,000	0.4
Arsenic (µg/L)	100	2.6	100	2.7	110	1.7	120	2.1	100	1.5	110	2.3
Selenium (µg/L)	130	11	120	8.8	130	3.3	160	5.3	110	7.0	130	6.4
Molybdenum (µg/L)	260	1.0	250	1.8	230	1.7	230	2.0	230	1.8	270	1.2
Silver (µg/L)	270	1.3	140	1.9	150	1.7	130	1.5	120	1.2	160	1.0
Cadmium (µg/L)	40	6.7	40	8.7	39	6.1	52	3.6	40	7.6	51	5.1
Mercury (µg/L)	44	3.9	1.4	45	3	8.8	<0.000	N/A	1	63	35	2.1
Lead (µg/L)	450	0.6	400	1.3	390	1.8	330	2.6	430	1.0	520	0.7

Table A7: Phase 1 Steady-State, Digester Set A and Feed Data

	(1 A)		(2 A)		Feed	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	7.18	6.91-7.28	7.17	7.09-7.31	5.86	5.54-6.37
TS, g/L	29.7	4.2	29.8	4.2	45.1	2.4
VS, g/L	20.6	2.8	20.5	2.8	35.4	1.6
VSR, %	42	9.2	42	8.8		
COD, g/L	31	4.1	32	7.4	58	2.2
sCOD, g/L	0.63	0.1	0.95	0.2	3	0.22
Alkalinity, mg/L as $CaCO_3$	3500	260	3500	370		
Methane, %	66.1	5.4	67.8	1.5		
Biogas Production, L/L-day	1.54	0.18	1.49	0.2		
VFAs, mg/L**	0	-	200	70	2900	610

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A8: Phase 1 Steady-State, Digester Set B and Feed Data

	(1 B)		(2 B)		Feed	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	7.2	7.09-7.31	7.2	7.10-7.32	5.79	5.54-6.21
TS, g/L	31.1	4.1	30.3	4	45.5	2.7
VS, g/L	21.1	2.9	20.5	2.6	35.4	1.8
VSR, %	40	6.9	42	9		
COD, g/L	35	5.4	32	4.7	60	3.6
sCOD, g/L	0.58	0.02	0.6	0.028	2.7	0.44
Alkalinity, mg/L as $CaCO_3$	3800	110	3900	190		
Methane, %	68.5	1.1	68.8	0.7		
Biogas Production, L/L-day	1.04	0.12	1.14	0.18		
VFAs, mg/L**	0	-	0	-	3100	620

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A9: Phase 1 Steady-State, Digester Set C and Feed Data

	(1 C)		(2 C)		Feed	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	7.22	7.11-7.35	7.21	7.10-7.32	5.79	5.54-6.21
TS, g/L	27.9	1.1	26.6	0.7	45.2	3.2
VS, g/L	18.7	0.9	17.9	0.5	35.4	2
VSR, %	47	5	49	3.4		
COD, g/L	32	1.7	30	1.9	57	4.8
sCOD, g/L	0.61	0.02	0.6	0.055	3	0.36
Alkalinity, mg/L as $CaCO_3$	4000	77	4000	170		
Methane, %	69.2	1.3	69.3	2.1		
Biogas Production, L/L-day	0.94	0.11	0.94	0.1		
VFAs, mg/L**	0	-	0	-	2800	580

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A10: Phase 1 Steady-State, Digester Set D and Feed Data

	(1 D)		Feed	
	Average	**Stdev**	**Average**	**Stdev**
pH	7.07	6.95-7.19	5.79	5.54-6.21
TS, g/L	31.5	0.7	45.5	2.7
VS, g/L	21.5	0.5	35.4	1.8
VSR, %				
COD, g/L				
sCOD, g/L				
Alkalinity, mg/L as $CaCO_3$	3500	130		
Methane, %				
Biogas Production, L/L-day				
VFAs, mg/L**				

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A11: Phase 2 Steady-State, Digester Set A and Feed Data

	(1 A)		(2 A)		Feed		Co-Digestate		Feed + Co-Di	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	7.08	6.81-7.21	7.02	6.86-7.16	5.82	5.42-6.28	5.99	5.45-6.65		
TS, g/L	26.9	1.2	26.1	1.4	45.9	4	27.4	2.8	42.4	2.4
VS, g/L	18.8	1	18.3	1.2	37.6	3.2	21.3	2.7	34.5	1.9
VSR, %	45	5.5	46	5.3						
COD, g/L	32.6	1.7	32.3	0.78					55.2	2
sCOD, g/L	0.45	0.033	0.44	0.022					3.2	0.44
Alkalinity, mg/L as $CaCO_3$	3700	420	3700	440						
Methane, %	68.5	1.3	68.7	1.2						
Biogas Production, L/L-day	1.82	0.23	1.8	0.21						
VFAs, mg/L**	0	-	0	-					2000	470

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A12: Phase 2 Steady-State, Digester Set B and Feed Data

	(1 B)		(2 B)		Feed		Co-Digestate		Feed + Co-Di	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	7	6.92-7.12	7	6.82-7.11	5.74	5.42-6.27	5.98	5.45-6.65		
TS, g/L	27	1.5	25.9	2.1	46	4.7	26.8	2.9	42.6	2.6
VS, g/L	18.6	1.4	17.9	1.6	37.9	3.6	20.7	2.8	34.3	2.2
VSR, %	45	5.2	48	7.4						
COD, g/L	28.1	6.8	31.4	3.2					56	2.9
sCOD, g/L	0.46	0.034	0.45	0.024					4.5	1
Alkalinity, mg/L as $CaCO_3$	4000	230	4100	350						
Methane, %	69.1	1.6	69.5	1.6						
Biogas Production, L/L-day	1.43	0.15	1.4	0.15						
VFAs, mg/L**	0	-	0	-					3200	720

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A13: Phase 2 Steady-State, Digester Set C and Feed Data

	(1 C)		(2 C)		Feed		Co-Digestate		Feed + Co-Di	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	7.03	6.93-7.15	7.06	6.96-7.21	5.68	5.42-6.00	5.96	5.45-6.65		
TS, g/L	25.6	2.1	25.8	2.4	48.6	3.1	25.8	2.8	43.9	2.1
VS, g/L	17.5	1.8	17.6	2	39.7	2.3	19.8	2.6	35.6	1.7
VSR, %	50	5.4	50	5.9						
COD, g/L	29.7	3.5	30.9	2.4					60.7	3.5
sCOD, g/L	0.48	0.04	0.48	0.04					6.2	0.28
Alkalinity, mg/L as $CaCO_3$	4400	200	4500	260						
Methane, %	70.2	1.6	70.2	1.4						
Biogas Production, L/L-day	1.09	0.08	1.09	0.08						
VFAs, mg/L**	0	-	0	-					4100	790

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A14: Phase 2 Steady-State, Digester Set D and Feed Data

	(1 D)		Feed		Co-Digestate		Feed + Co-Di	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	6.99	6.86-7.10	5.74	5.42-6.27	5.98	5.45-6.65		
TS, g/L	26	1.3	46	4.7	26.8	2.9	42.6	2.6
VS, g/L	18.4	0.8	37.9	3.6	20.7	2.8	34.3	2.2
VSR, %	46	2.4						
COD, g/L								
sCOD, g/L								
Alkalinity, mg/L as $CaCO_3$	3800	420						
Methane, %								
Biogas Production, L/L-day								
VFAs, mg/L**								

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A15: Phase 3 Steady-State, Digester Set A and Feed Data

	(1 A)		(2 A)		Feed		Co-Digestate		Feed + Co-Di	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	6.88	6.77-7.04	6.83	6.70-6.99	5.83	5.68-6.02	5.71	5.41-5.89		
TS, g/L	21.8	2.4	21.3	3.2	49.9	2.4	20.9	1.2	37.3	1.9
VS, g/L	14.9	1.8	14.5	2.4	40.9	2.5	16.7	1.4	30.3	1.6
VSR, %	51	5.4	52	6.5						
COD, g/L	29.2	1.6	29	2.4					55.2	3.2
sCOD, g/L	0.6	0.05	0.71	0.05					4.5	0.23
Alkalinity, mg/L as $CaCO_3$	3000	250	2900	250						
Methane, %	68.2	2.3	67.4	2.5						
Biogas Production, L/L-day	1.96	0.1	2.03	0.13						
VFAs, mg/L**	0	-	150	70					3600	900

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A16: Phase 3 Steady-State, Digester Set B and Feed Data

	(1 B)		(2 B)		Feed		Co-Digestate		Feed + Co-Di	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	6.82	6.72-6.93	6.85	6.75-6.97	5.79	5.68-5.90	5.72	5.62-5.85		
TS, g/L	20.4	3	20.7	3	49.9	2.4	20.9	1.2	36	1.9
VS, g/L	13.5	2.1	13.8	2.1	40.9	2.5	16.7	1.4	29.2	1.9
VSR, %	53	11	53	12						
COD, g/L	24.3	3	25.4	1.8					47.4	2.5
sCOD, g/L	0.43	0.04	0.45	0.03					3.4	0.79
Alkalinity, mg/L as $CaCO_3$	3200	160	3200	200						
Methane, %	67.5	2.6	67.3	2.6						
Biogas Production, L/L-day	1.62	0.15	1.61	0.15						
VFAs, mg/L**	0	-	0	-					2700	610

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A17: Phase 3 Steady-State, Digester Set C and Feed Data

	(1 C)		(2 C)		Feed		Co-Digestate		Feed + Co-Di	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	6.83	6.77-6.92	6.86	6.80-6.98	5.82	5.71-5.90	5.71	5.63-5.75		
TS, g/L	21.2	0.8	22.2	0.6	49.9	2.4	20.9	1.2	37	1.7
VS, g/L	14.1	0.6	14.5	0.5	40.9	2.5	16.7	1.4	30.3	1.5
VSR, %	53	3	52	4						
COD, g/L	25.1	0.61	26	1.2					48.7	2
sCOD, g/L	0.46	0.025	0.47	0.04					3.4	0.3
Alkalinity, mg/L as $CaCO_3$	3100	40	3200	40						
Methane, %	66.9	0.9	64.5	1.3						
Biogas Production, L/L-day	1.29	0.15	1.4	0.17						
VFAs, mg/L**	56	50	0	-					2200	500

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A18: Phase 3 Steady-State, Digester Set D and Feed Data

	(1 D)		Feed		Co-Digestate		Feed + Co-Di	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	6.82	6.72-6.95	5.79	5.68-5.90	5.72	5.62-5.85		
TS, g/L	21.2	1.2	49.9	2.4	20.9	1.2	36	1.9
VS, g/L	14.6	1	40.9	2.5	16.7	1.4	29.2	1.9
VSR, %								
COD, g/L								
sCOD, g/L								
Alkalinity, mg/L as $CaCO_3$	2800	250						
Methane, %								
Biogas Production, L/L-day								
VFAs, mg/L**								

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A19: Phase 4, Digester Set A and Feed Data

	(1 A)		(2 A)		Feed		Co-Digestate		Feed + Co-Di	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	6.79	6.50-6.95	6.71	6.56-6.99	6.22	6.02-6.50	5.39	4.32-6.13		
TS, g/L	23.3	0.39	25.3	0.78	47.3	0.6	28.2	0.4	37.8	0.42
VS, g/L	15.3	0.4	17	1	38.4	0.5	17.6	0.9	28	0.61
VSR, %	45	5	39	7						
COD, g/L										
Biogas Production, L/L-day	2.4	0.03	1.4	0.06						
VFAs, mg/L**	55	30	5200	1500	2500	480	1400	470		

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A20: Phase 4, Digester Set B and Feed Data

	(1 B)		(2 B)		Feed		Co-Digestate		Feed + Co-Di	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	6.46	5.42-7.05	6.39	5.28-7.04	6.22	6.02-6.50	5.39	4.32-6.13		
TS, g/L	22.3	0.76	22.1	1.21	47.3	0.6	28.2	0.4	35.3	0.39
VS, g/L	14.5	0.5	14.6	0.6	38.4	0.5	17.6	0.9	25.3	0.67
VSR, %	43	5	43	4						
COD, g/L										
Biogas Production, L/L-day	0.59	0.16	0.54	0.14						
VFAs, mg/L**	11000	2500	14000	3200	2500	480	1400	470		

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A21: Phase 4, Digester Set C and Feed Data

	(1 C)		(2 C)		Feed		Co-Digestate		Feed + Co-Di	
	Average	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**	**Average**	**Stdev**
pH	6.71	6.58-7.05	6.73	6.61-6.92	6.22	6.02-6.50	5.39	4.32-6.13		
TS, g/L	18.9	0.93	19.4	0.7	47.3	0.6	28.2	0.4	34.5	0.38
VS, g/L	11.5	0.3	11.9	0.4	38.4	0.5	17.6	0.9	24.5	0.69
VSR, %	53	5	51	6						
COD, g/L										
Biogas Production, L/L-day	2.17	0.01	1.76	0.08						
VFAs, mg/L**	670	260	2700	1000	2500	480	1400	470		

*Duplicate digesters were statistically different

**Total VFAs as Acetic Acid

Table A22: Phase 1, Dewatering Test Results

Technology	Polymer Type	Polymer Dose, active lb/dry ton	Maximum Achievable Cake Solids Concentration, % TS
Piston Press[1]	BASF 7557	18.5	28
J-Vap	Praestol K290FLX	16.5	25
Centrifuge	SNF Polydyne C6267	28.5	22.6
Centrifuge	Ashland K-290FLX	25.6	21
Centrifuge	290FLX	21.6	20

[1]Dehydris Twist Piston Press

Table A23: Phase 2, Dewatering Test Results

		Unheated Sample		Heated Sample	
Technology	Polymer Type	Polymer Dose, active lb/dry ton	Maximum Achievable Cake Solids Concentration, % TS	Polymer Dose, active lb/dry ton	Maximum Achievable Cake Solids Concentration, % TS
Centrifuge	K290 FLX	23-27	21.5	23-30	21.7 [c]
Centrifuge	C6287	24-26	21	37	21 ± 2 [a]
Centrifuge	BASF Z8848FS	16.8	20	19.2	21.7 ± 2 [b]

[a]Test temperature: 60°C

[b]Test temperature: 55-70°C

[c]Test temperature: 60°C

Table A24: Calorimetry Results for Total Solids

	BTU/g total solids			
	Phase 1		Phase 2	
	Average	STDEV	Average	STDEV
Vendor 1	17.2	3.5	16.5	0.92
Vendor 2	17.2	2.8	16.5	0.05
Vendor 3				
Vendor 4			15.6	1.2

Table A25: Calorimetry Results for Volatile Solids

	BTU/g volatile solids			
	Phase 1		Phase 2	
	Average	STDEV	Average	STDEV
Vendor 1	24.6	5	21.8	1.2
Vendor 2	24.5	4.1	21.8	0.07
Vendor 3	19.5	0.44		
Vendor 4	24.5	0.12	20.9	1.6

Table A26: BMP Results for Individual Wastes

Waste	Average (mL CH_4/g COD)	Stdev
Co-digestate Mix	350	15
Co 1-Vegetable Blancher Water	310	3.6
Co 4-Cheese Production DAF Tank Sludge	280	16
TPS	250	32
TPS	240	19
Municipal Feed	220	3
Co 2-Milk Processing Wash Water	210	6.2
Co 3-Cheese Production DAF Tank Sludge and Float	200	36
TWAS	130	4.9
TWAS	120	68

Table A27: BMP, Theoretical and Observed Results

	Theoretical		Observed	
	Average (mL CH_4/g COD)	Stdev	Average (mL CH_4/g COD)	Stdev
Co 2-Milk Processing Wash Water	210	4.3	270	2.3
Co 3-Cheese Production DAF Tank Sludge and Float	210	19	230	2.0
Co 4-Cheese Production DAF Tank Sludge	250	12	260	7.3
Co 1-Vegetable Blancher Water	270	11	270	19
Co-digestate Mix	280	11	280	7.3

Table A28: Phase 1 Siloxane Concentrations

	(1 A)		(2 A)		(1 B)		(2 B)		(1 C)		(2 C)	
	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
Total (Si, mg/m^3)	1.6	0.32	1.3	1.1	0.91	1.3	0.10	0.03	1.0	0.10	1.8	1.0

Table A29: Phase 2 Siloxane Concentrations

	(1 A)		(2 A)		(1 B)		(2 B)		(1 C)		(2 C)	
	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
Total (Si, mg/m^3)	1.7	0.27	1.2	0.03	1.5	0.14	1.0	0.29	2.3	0.93	1.3	0.21

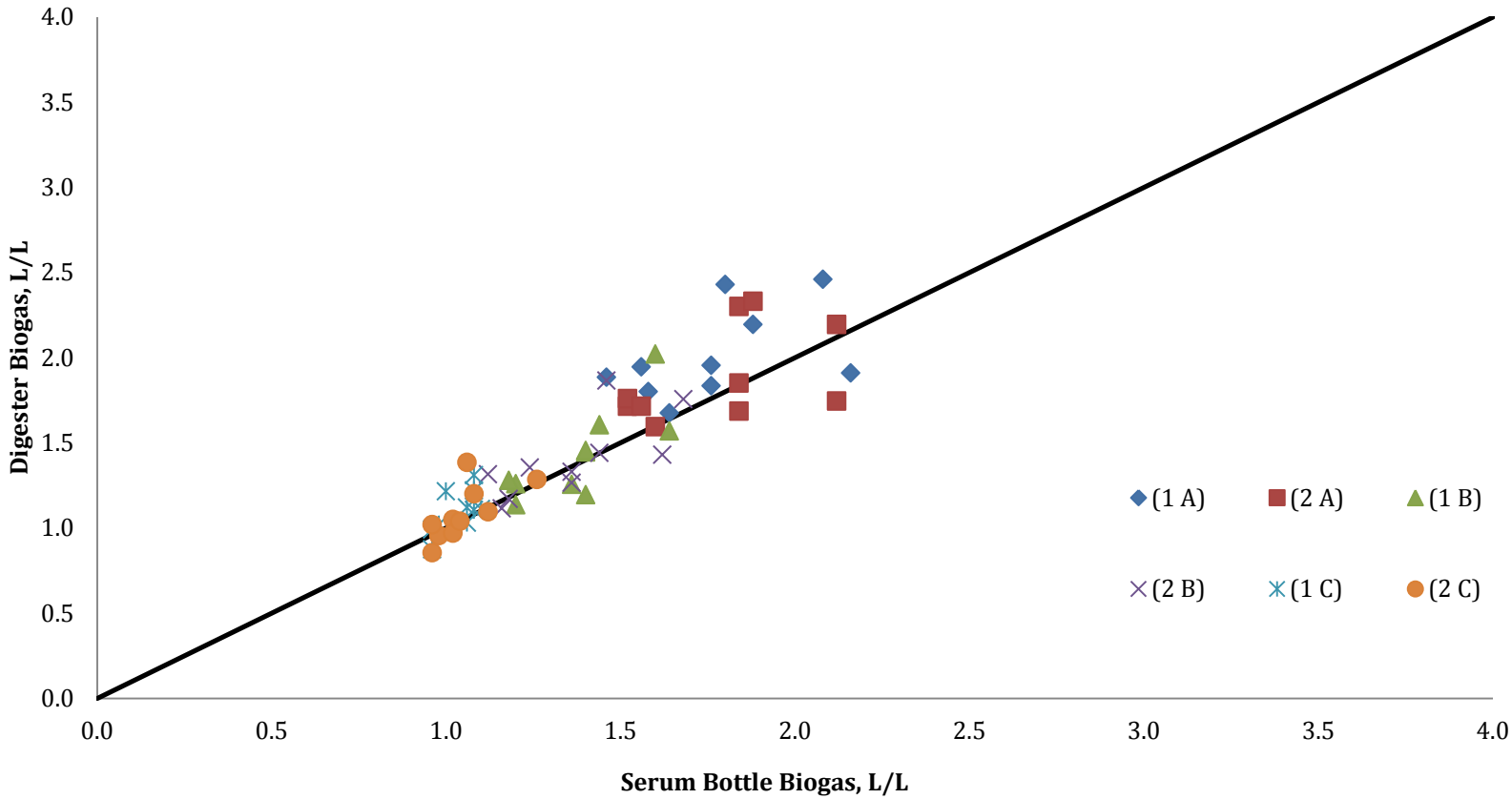

Figure A1: Phase 2 Serum Bottle Biogas and Digester Biogas Production Relationship

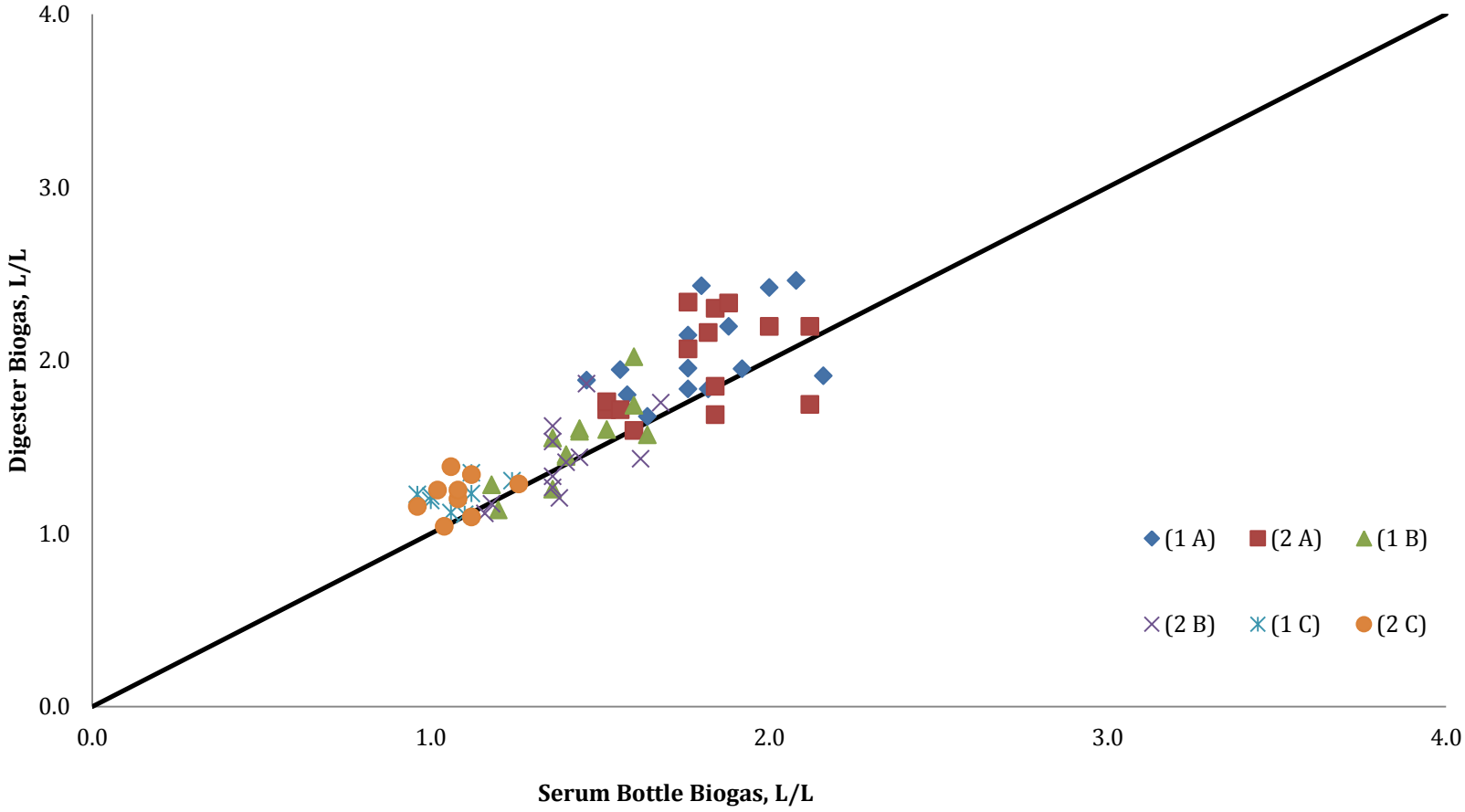

Figure A2: Phase 3 Serum Bottle Biogas and Digester Biogas Production Relationship

Gas Quality and Measurement of Landfill Gas and Bio-gas – Application No 1.

SILOXANES AND MEASUREMENT

TOTAL AND SPECIATION OF VOLATILE ORGANIC SILICON IN FUEL GASES BY GAS CHROMATOGRAPHY-ATOMIC EMISSION DETECTOR

The presence of volatile organosilicon compounds in landfill gas was known to cause catastrophic combustion engine failure due to the formation of abrasive microcrystalline silica. A sensitive and ready method is required to quantitate the total silicon content and individual species. The total silicon measurement provides one of the most critical fuel-gas quality parameter. Speciation provides information on the type, the amount and the distribution of various organosilicon compounds present in landfill gas. This information is of a great value to the utilization of landfill gas and other biogases for energy production and to the development and evaluation of clean-up processes.

A direct measurement method was developed and extensively utilized for last six years. The volatile organic silicon-containing compounds in biogas are separated by gas chromatography (GC) techniques and subsequently detected by an atomic emission detector (AED) using a microwave-induced He plasma (HIP). The characteristic emissions from silicon (Si-252 nm) and carbon (C-248 nm) of each component are simultaneously monitored for compound confirmation and measurement. The gas sample is collected in inert container and directly injected onto GC-AED using a fixed sampling loop for qualitative and quantitative measurement. The detection limit of each silicon compound is approximately 0.1-0.01 ppmv as silicon. Target organic silicon species include tetramethyl silane, trimethyl silanol, linear (L2-L5) and cyclic siloxanes (D3-D6). Other organic silicon species are detected together and reported as "others" or "unidentified". The total volatile organic silicon is measured by the total Si emission or the sum of all organic silicon species.

The GC-AED technique has noted advantages of sensitivity, selectivity and compound-independent calibration technique over GC-MS. The sensitivity of GC-AED is better than most quadruple GC-MS'. The selectivity allows easy identification of all organic silicon compounds. The compound-independent calibration (CIC) technique enables accurate measurement of target or unidentified organic silicon compounds using only one stable organic silicon compound as the standard. The CIC technique can be employed for calibration at C-248 nm, simultaneously. This allows measurements of NMHC (Non-Methane Hydrocarbon) and hydrocarbon (boiling point) distribution.

Sound siloxane sampling is critical to the accurate measurement. Grab sampling can be done easily and quickly with stainless steel cylinder, silica-coated steel cylinder or Tedlar bag. The entire sampling system must be conditioned well and good sampling technique must be followed for representative grab sampling. Normally, only a small amount of LFG (0.5-1 liter) is required, but a larger volume can improve overall sampling and measurement reliability. On-site methanol impinger method has the advantages of time-weight-average (TWA) sampling, but it is a tedious process and the fate of siloxanes in methanol is unknown and may vary from LFG to LFG. Carbon trap can also be used instead of methanol to collect siloxanes for subsequent thermal desorption and GC analysis. GC-AED method can be employed for both grab gas or trap samples using methanol or carbon.