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Upflow Anaerobic Sludge Blanket Reactors for Treatment of Wastewater from the Brewery Industry

by

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S.B. Materials Science and Engineering
Massachusetts Institute of Technology, 2009

SUBMITTED TO THE DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING ON DECEMBER 11, 2009 IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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ABSTRACT

Anaerobic digestion can be utilized to convert industrial wastewater into clean water and energy. The goal of this project was to set up lab-scale anaerobic digesters to collect data that will be used to develop and validate a predictive monitoring and controls solution to improve digester performance. The research project involved the design, construction, and instrumentation of lab-scale anaerobic digestion reactors to be used for the treatment of brewery wastewater. Useful parameters for monitoring the health of the digesters were identified and techniques for measuring each parameter were evaluated to determine the best analytical methods. A synthetic brewery wastewater was prepared and the reactors were operated until a stable steady-state was achieved. Data was collected to evaluate the anaerobic digesters from start-up to steady-state, and controlled variations were implemented in order to obtain transient data for the supervisory model. Initial perturbations in organic loading rate and influent pH suggest that gas composition and gas production appear to be the best on-line monitoring parameters to indicate changes in reactor conditions.

Thesis Supervisor: Angela Belcher

Title: Professor of Materials Science and Engineering and Biological Engineering

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COD – Chemical Oxygen Demand
HRT – Hydraulic Retention Time
OLR – Organic Loading Rate
SCOD – Soluble Chemical Oxygen Demand
SRT – Solids Retention Time
TCOD – Total Chemical Oxygen Demand
TOC – Total Organic Carbon
UASB – Upflow Anaerobic Sludge Blanket
VFA – Volatile Fatty Acid

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Introduction

Waste to Value

In today's society, energy and water costs are rising, clean water is becoming less available, and environmental regulations for wastewater discharge are becoming increasingly stringent. GE Water and Process Technology's Waste to Value initiative addresses these issues by focusing on extracting energy and clean water from wastewater for industrial re-use. The Waste to Value processing solution will convert wastewater into clean water and biogas, which can be used as an energy source, thereby reducing fossil fuel based energy consumption, reducing green house gas emissions, and reducing fresh water intake (Figure 1).

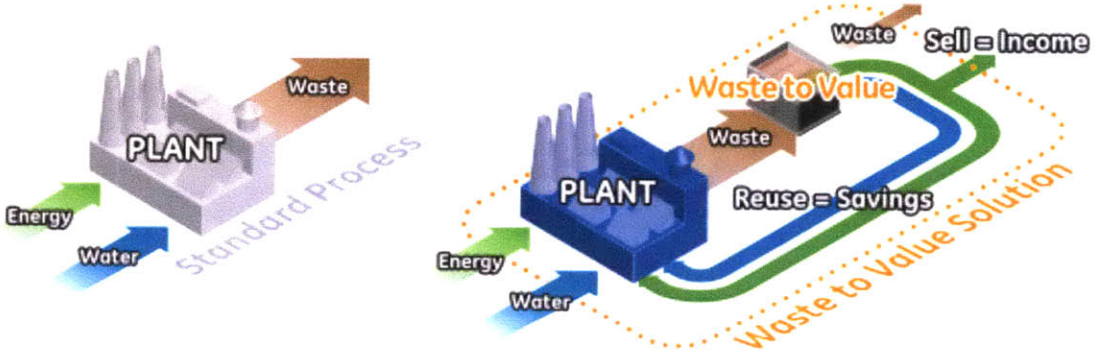

Figure 1. Advantages of Waste to Value Solution compared to standard wastewater treatment processes. Image from GE Waste to Value brochure and reprinted with permission from Paul Valeck, GE Water and Process Technologies. Copyright General Electric Company, 2009.

Supervisory Controls

One key challenge to successfully implementing the Waste-to-Value solution in industrial plants is maintaining a stable, reliable process without frequent upsets and shutdowns for maintenance. The overall Waste-to-Value system includes several components. The first step in the process is anaerobic digestion, where organics in the wastewater are broken down to produce clean water and biogas. In subsequent steps, the water is further treated through aerobic reaction and filtration, and the biogas undergoes further processing and finally combustion in a boiler or engine (Figure 2).

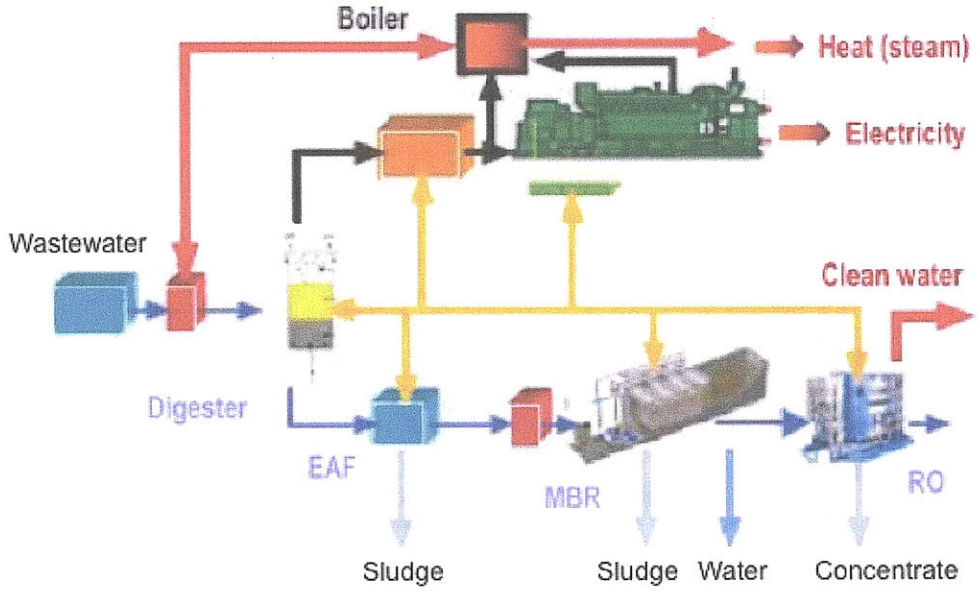

Figure 2. Waste to Value plant. Reprinted from U.S. Department of Energy, Energy Efficiency and Renewable Energy Industrial Technologies Program, Flexible Distributed Energy and Water from Waste for the Food and Beverage Industry.

The first process step, anaerobic digestion, is a sensitive and complex process involving balanced interactions between many different microorganisms. Any problems or upsets in this process will have an effect on all subsequent processing steps,

significantly impacting the entire plant's performance. GE also sells all the equipment used downstream of the anaerobic digester but is not currently involved in the digester business. Therefore, it is necessary to gain expertise in the area of anaerobic digestion and to develop ways to better predict and mitigate process upsets.

The overall goal of this project, funded by the Department of Energy, is to develop a monitoring and supervisory controls system to better control the overall system, including the anaerobic digestion process. The solution will ensure robust and stable operation of the overall system by understanding, detecting, and controlling potential upsets.

Internship Master's Thesis Overview and Goals

The goal of this Master's internship was to set up lab-scale anaerobic digesters to collect data that will be used to develop and validate a model for a predictive monitoring and controls solution to improve digester performance. The thesis research was performed in collaboration with Professor Lars Angenent at Cornell University, who provided first-hand experience on brewery wastewater treatment as well as setting up and running anaerobic digesters. The research project involved the design, construction, and instrumentation of lab-scale anaerobic digestion reactors both at the GE Global Research Center and at Cornell University. Useful parameters for monitoring the health of the digester were identified and different techniques for measuring each parameter were explored and evaluated to determine the best analytical methods. Once the reactors started running, data was collected to evaluate the anaerobic digesters from start-up to steady state, as well as in response to varying environmental and operational conditions.

In this project, controlled variations will be implemented in order to obtain steady state and transient data for the model, and data will be evaluated to understand the reactor performance under a wide range of conditions. The data generated in these experiments will be essential to validate predictive models and to identify which experimental variables are the best indicators of process upset.

Background and Literature Review

Advantages of Anaerobic Digestion

Over the past two decades, anaerobic digestion has emerged as a sustainable technology for wastewater treatment. In comparison to traditional aerobic wastewater treatment, anaerobic digestion has several advantages. Anaerobic digestion is considered an inexpensive process because it requires relatively simple reactors and operation requires relatively small reactor volumes and little energy consumption.[1] In fact, anaerobic digestion converts organics in industrial wastewater into methane gas, which can be used for energy, as compared to the aerobic treatment process, which is very energy intensive.[2] In aerobic treatment processes, 50% of incoming organics in the wastewater are converted into new biomass, or sludge, that has high disposal costs. In contrast, anaerobic digesters only convert 10% of incoming COD to biomass, which significantly cuts costs for sludge disposal. The anaerobic digestion process also has lower nutrient requirements and no oxygen requirement. Anaerobic digesters are often followed by an aerobic polishing step to remove solids, nitrogen, and phosphorus to provide a high quality effluent that will meet strict discharge requirements.

Despite these advantages, there is resistance in the United States to adopt anaerobic digestion technology for wastewater treatment. The anaerobic digestion process has a reputation of being very unstable, especially when dealing with load variations. However, Lettinga states in his review of anaerobic digestion technology: "many upsets of anaerobic digestion systems in the past could be attributed to a lack of knowledge of the basic principles of the process. As a matter of fact, the anaerobic digestion is highly stable, provided the system is operated in the proper way. This means that the process should be sufficiently understood by engineers and operators."[3] A predictive monitoring and controls solution would help operators and engineers to operate their systems properly and increase overall confidence in the anaerobic digestion process, which could promote adoption and acceptance of the technology.

Wastes from the food and beverage industry are likely to be anaerobically digestible, making it an ideal industry for anaerobic digestion. Breweries in particular have traditionally been more willing to adopt new wastewater treatment technologies because they consume large quantities of water in their processing operations.[4] Breweries consume 4 to 11 liters of water for every liter of beer produced, with 2/3 of the water consumed in the brewing process and 1/3 in the cleaning processes.[5] The wastewater produced through the brewing process is a great candidate for anaerobic digestion because it contains readily degradable components like sugars, ethanol, and volatile fatty acids.

The Anheuser-Busch brewery in Baldwinsville, NY is one brewery that adopted anaerobic digestion as part of its wastewater treatment process approximately 20 years ago. Since then, the plant has been able to offset 19% of its energy costs through various

energy conservation efforts, and was able to reduce wastewater treatment power requirements by 60%. The plant also significantly reduced carbon dioxide emissions. [6,7]

Anaerobic Digestion Technology: Upflow Anaerobic Sludge Blanket (UASB) Reactors

Several types of anaerobic digestion reactors exist for wastewater treatment, but one that is widely used in the brewery industry in particular is the Upflow Anaerobic Sludge Blanket (UASB) reactor (Figure 3). This high-rate anaerobic digestion reactor has been increasingly implemented in industry for anaerobic treatment of wastewater. Influent wastewater enters the cylindrical reactor through an inlet at the bottom of the reactor and passes through a feed distribution system that distributes throughout the cross-section of the reactor. The reactor is filled with granules, approximately 1-5 mm in diameter, consisting of a layered consortia of different anaerobic bacteria. These granules of bacteria and extracellular polymeric substance, also called sludge or biomass, degrade the organics in the wastewater and produce methane gas. The hydraulic upflow of the wastewater flowing into the reactor keeps the granules in a partially fluidized state. Mechanical mixing is not necessary because hydraulic upflow and biogas production provide sufficient mixing of the reactor contents. At the top of the reactor, the water and biogas reach an inverted cone gas-liquid-solid separation system. The biogas is collected in the inverted cone and the solids settle back down in the reactor, which reduces biomass washout. The treated effluent is discharged, and a portion of the treated effluent is recycled back into the reactor to aid in reactor mixing.[8] Variation of the recycle rate also allows for variable influent flow.

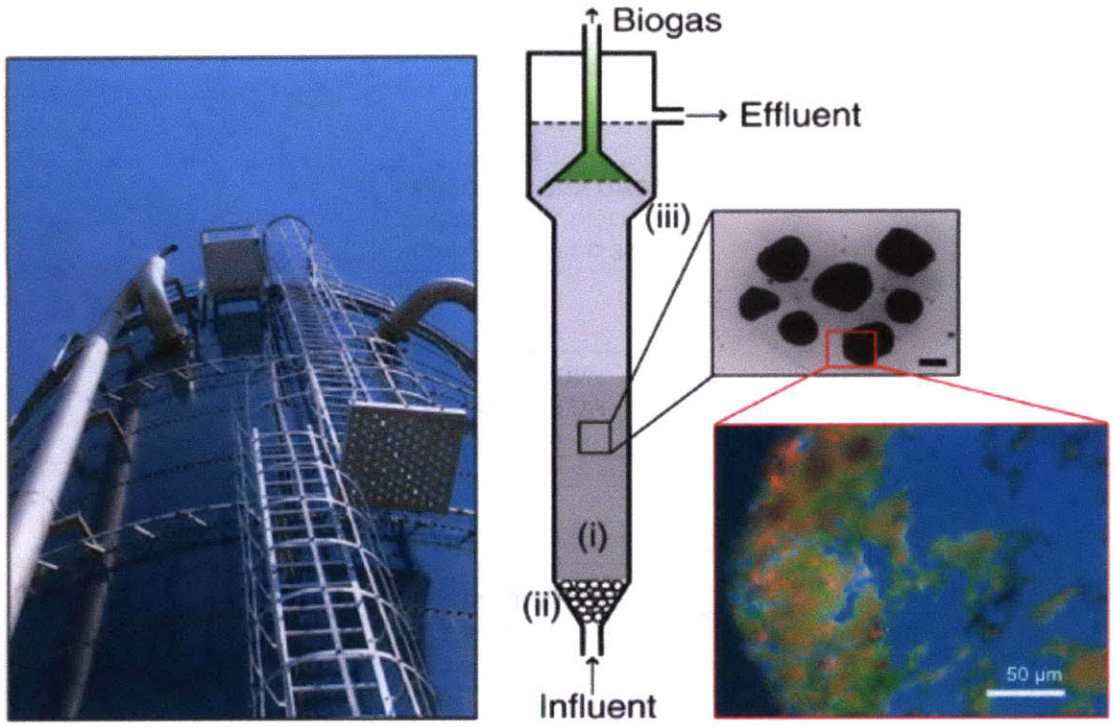

Figure 3. Upflow Anaerobic Sludge Blanket (UASB) Reactor: Full-scale Biothane reactor, granules, and granule structure. Figure reprinted by permission from Macmillan Publishers Ltd: [NATURE IMMUNOLOGY] (Sonnenburg, J.L., Angenent, L.T., and Gordon, J.I. Getting a grip on things: how do communities of bacterial symbionts become established in our intestine? Nature Immunology (2004) Vol. 5 No. 6., pp. 569-573.), Nature Publishing Group (2004). Full-scale reactor photo reprinted with permission from Biothane, LLC. Granule structure photo from D. Zheng, L.T. Angenent, L. Raskin; Copyright 2006 Wiley Periodicals, Inc.; Reprinted with permission of Wiley-Liss, Inc. a subsidiary of John Wiley and Sons, Inc.

The Anaerobic Digestion Process

The anaerobic digestion process involves four main steps (Figure 4). The first step is the hydrolysis of carbohydrates, proteins, and fats into sugars, amino acids, and fatty acids that are available for bacteria. In the second fermentation step, acidogenic bacteria convert these soluble organic molecules into acetic acid, volatile fatty acids, hydrogen, and carbon dioxide. Approximately 51% of the organics will be converted to

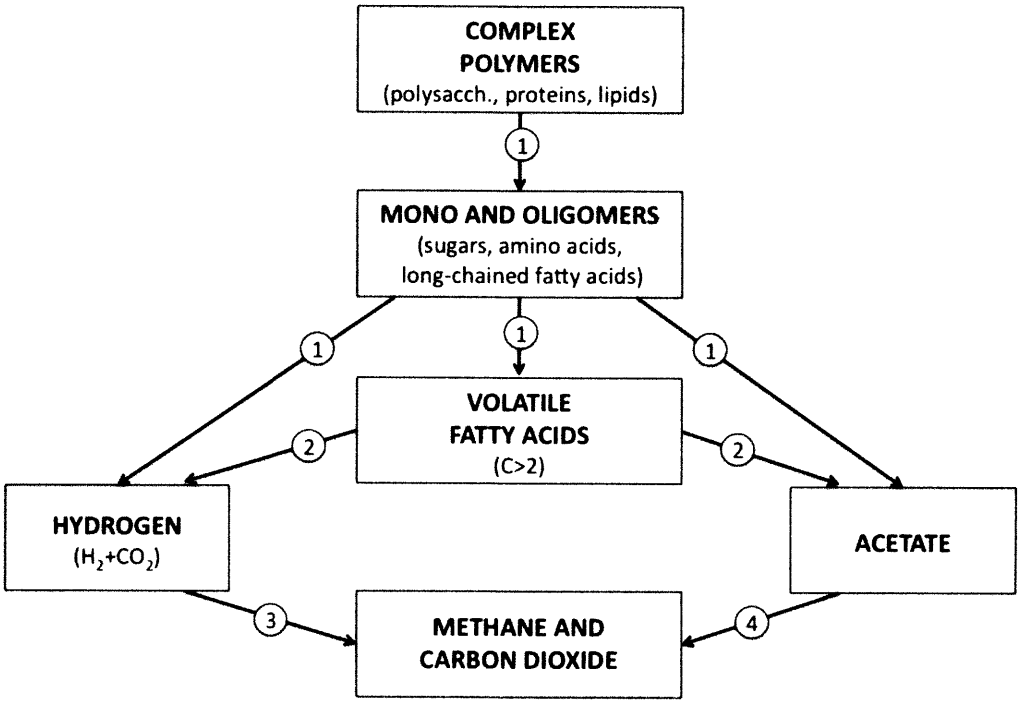

Figure 4. Anaerobic Digestion Process. Figure reprinted from Biomethanation I, Volume 81, 2003, Page 3, Perspectives for Anaerobic Digestion, Advances in Biochemical Engineering/Biotechnology Series, Birgitte K. Ahring, Figure 1, Copyright 2003 Springer Berlin/Heidelberg with kind permission of Springer Science+Business Media.

acetic acid, 30% will be converted to other volatile fatty acids, and 19% will be converted to hydrogen and carbon dioxide (Figure 5).[10] In the third step, acetogenic bacteria convert the volatile fatty acids into acetic acid or hydrogen and carbon dioxide, and in the final step, methanogens convert these products into methane and carbon dioxide. There are at least two different populations of methanogens. Acetoclastic methanogens convert acetate to methane, and hydrogenotrophic methanogens use hydrogen to reduce carbon dioxide to methane. Stable anaerobic digestion depends on keeping this process in balance, meaning balance must be achieved between acid-forming and methane-forming bacteria.

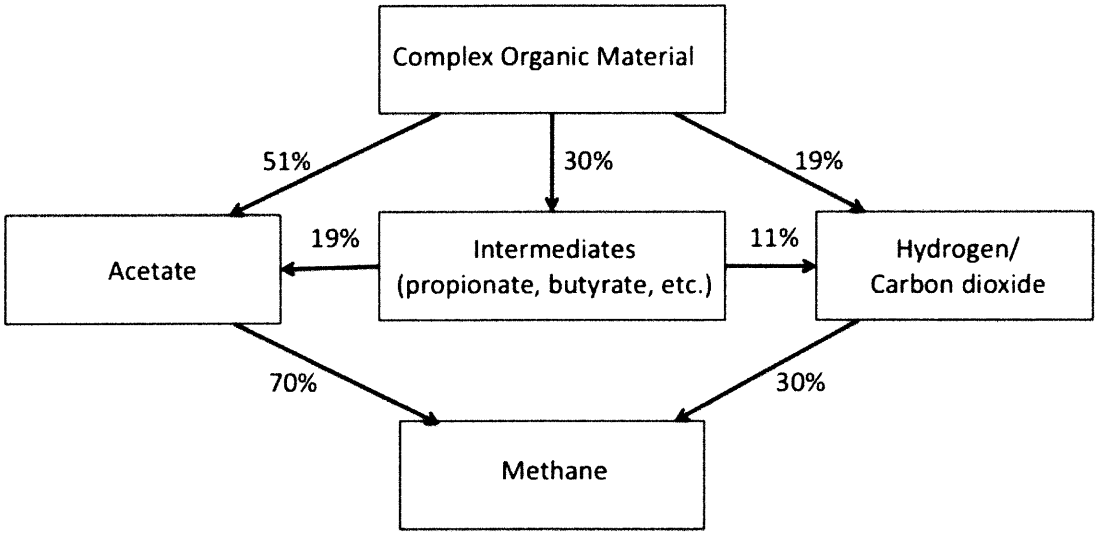

Figure 5. Different pathways for breakdown of complex organic material through anaerobic digestion. Figure reprinted from Biomethanation I, Volume 81, 2003, Page 4, Perspectives for Anaerobic Digestion, Advances in Biochemical Engineering/ Biotechnology Series, Birgitte K. Ahring, Figure 2, Copyright 2003 Springer Berlin/Heidelberg with kind permission of Springer Science+Business Media.

Theories of Granule Formation

It is the granular consortium of microorganisms that gives the UASB reactor its operational advantages.[11] The granules comprising the sludge blanket are densely packed, near-spherical structures of microorganisms. As indicated in Figure 3, the granules have a characteristic layered structure in order to maximize substrate utilization and to promote syntrophic bacterial relationships. During the granulation process, methanogens form the nuclei and other microorganisms attach to these nuclei and proliferate, forming dense aggregates. The hydraulic upflow is slowly increased in order to washout those organisms that are not capable of attaching, ultimately leading to the selection of granules with superior settling properties. In the typical layered granule structure, the outside layer is comprised of acidogens, and methanogens are within the

center of the sphere. However, this structure will vary with different feedstocks. It is suggested that this layered structure and close association between acetogens and methanogens promotes their synthrophic relationship by promoting substrate diffusion and hydrogen transfer.[12] Because granules have excellent settling properties, they tend to be retained in the reactor. As a result, the solids retention time is uncoupled from the hydraulic retention time.[13]

After decades of research, there is still no consensus on the chemical, physical, and material interactions that govern granulation. Many different theories exist to explain the granulation phenomenon, and the existing theories can be grouped into three different categories: physical, microbial, and thermodynamic.[14] The physical theories explain granulation based on conditions in the reactor, including liquid and gas flow and sludge properties like size and density.[15] Microbial theories of granulation focus on specific microorganism properties, such as the production of extracellular polymers and amino acids by certain microorganisms and not others.[16] Others propose that certain methanogens with good adhesion properties and the ability to secrete extracellular polymers serve as nuclei to which other microorganisms can attach.[17] The nucleus then grows to promote syntrophic relationships. Some researchers think that this is not governed solely by physical conditions or random aggregation, but that "bacteria search for strategic positions for supply of substrates and for removal of products."[18]

The final set of thermodynamic theories explain granule formation in terms of the adhesion energy and physico-chemical interactions between cells and between cells and other surfaces.[19] In one such theory, cells are transported to the surface of another cell by diffusion or fluid and gas flow. An initial adsorption occurs based on calculated Gibbs

free energy of adhesion, given that at a certain distance cells experience a weak attraction based on secondary ionic, dipolar, hydrogen, or hydrophobic interactions. At this distance there is a minimum in free energy and reversible adsorption occurs.[20] The next step is irreversible adhesion based on surface properties of the cell, and finally growth within the granule results in the formation of a dense, spherical consortia of microorganisms with ideal settling properties.

Despite many different theories explaining granulation, researchers agree on a few important points. Acetate-utilizing methanogens are critical for granule formation, and the first stage of granulation is bacterial adhesion, whether it is determined by physical, microbial, or thermodynamic properties. Experiments both at the lab- and full-scale have also shown that washout of lighter particles to select for growth of heavier, dense, better settlers is key to achieving good granules and good reactor performance. Finally, granulation depends on the growth and multiplication of different microorganisms within the consortia.[21]

Stability of Anaerobic Digesters

The stable anaerobic digestion process depends on keeping the process in equilibrium, and balance must be achieved between acid-forming and methane-forming bacteria to maintain granular structure and to keep the UASB reactor functioning efficiently. If there is a change in environmental or process conditions in the reactor, this change may inhibit methanogenic microorganisms, and methanogens will not use up acids and hydrogen as quickly as they are produced. Acidogens are typically more robust and can survive in a wider pH range compared to methanogens, which are the most

sensitive microorganisms and have the slowest growth rate.[22] In the case of instability, methanogens cannot keep up with the acid-producers and volatile fatty acids will typically build up in the reactor. This build up in volatile fatty acids will reduce the bicarbonate alkalinity in the reactor, and the pH in the reactor will decrease. This decrease in pH will further favor the acid-producers, resulting in the production of more VFAs and further inhibition of methanogens.

In addition, under upset conditions, an imbalance between the microorganisms within the granules will cause the granules to disintegrate, float, and wash out of the reactor, which is extremely detrimental to reactor performance.[23] This occurs when acid-producing microorganisms on the outer layers of the granules are favored. When the granules get too large and methanogens are buried deep inside, gas bubbles get trapped in the center of granules, and the buoyant force of these bubbles carries the granules to the surface.[24]

Leitão et al. recently summarized the causes, types, and effects of operational and environmental variations on anaerobic wastewater treatment systems, including UASB reactors. The review discussed the effects of many different environmental variations on different systems, including hydraulic and organic load variations, temperature variations, pH variations, and shocks with specific compounds, as well as effects of duration and frequency of variations.[25] Looking at the research to date on stability of anaerobic digesters, it is clear that reactor performance depends on the type, magnitude, duration, and frequency of the variation. The highlights of this review article are presented here.

Hydraulic and Organic Load Variations

Variations in hydraulic load will affect the dynamics of the sludge bed, depending on equilibrium between the upflow velocity and the sludge settling velocity. It is necessary to maintain a constant linear upflow velocity, typically less than 1 meter/hour. In the case of higher hydraulic load, granules may disintegrate under shear forces and lighter, less dense biomass will wash out in the effluent. If hydraulic flow is too low, the treatment capacity will deteriorate because the contact between the sludge granules and substrate will be insufficient. Variations in organic loading also have an impact on reactor performance and granules. In conditions of underloading, filamentous microorganisms will proliferate over others because they have a higher surface area to volume ratio and may have a competitive advantage in underload conditions.[26] In conditions of overloading, VFA production and gas production increase until methanogens cannot eliminate all the acids and hydrogen from the liquid and the process is inhibited.

Wastewater Composition

Others have looked at the stability of anaerobic digesters degrading wastewaters with different compositions, such as varying concentrations of VFAs and carbohydrates. Since the microorganisms that degrade sugars and produce acids are faster growers than methanogens, a wastewater that is primarily composed of carbohydrates will promote the growth of acid-producers. Therefore, in order to cultivate a strong population of methanogens, especially during start-up, it is better to feed a combination of sugars and VFAs. Several experiments have been performed with varying wastewater compositions.

Wong et al. fed four lab-scale UASB reactors with different compositions of VFAs, and found that different compositions of VFAs impacted reactor performance, with feeds containing acetate and butyrate resulting in better performance, and propionate substrate causing reactor failure.[27] In addition, Elias et al. looked at two lab-scale UASB reactors, one fed with VFAs and the other fed with glucose. The reactor operating on an acidified substrate recovered more quickly from instabilities than the reactor operating on glucose, likely because it had a strong methanogen population. The acidified substrate also reduced flotation and biomass washout.[28] Xing et al. studied more long-term periodic substrate perturbations with varying glucose in the substrate on a 6-day cycle. The community proved to be sensitive to the fluctuations, with periodic build up of intermediates, but eventually the system reached a new steady state after giving the microorganisms 300 days to adapt.[29]

Temperature

Temperature is an important parameter in the anaerobic digestion process because it dictates the speed of chemical reactions. There are three different temperature ranges within which anaerobic digestion proceeds: Psychrophilic (below 20 °C). Mesophilic (20-40°C), and Thermophilic (40-70°). Most commonly, digesters are operated in the Mesophilic range, at an optimum temperature of 35-37°C. When temperature fluctuates, different microorganisms respond differently and this can upset the digestion process. Temperature decreases slow down all reactions and microbial activity, which can result in the accumulation of VFAs and a decrease in pH. Temperature increases typically increase microbial activity until the decay rate of the microorganisms exceeds the growth

rate, at which point reactor performance decreases. Variations in temperature can also affect the sludge bed because temperature changes will change viscosity and therefore shear forces on the granules.[30] Psychrophilic, Mesophilic, and Thermophilic conditions typically involve a consortium of different species and it can take months for the consortium to acclimatize. Therefore, in contrast to short-term temperature fluctuations, under long-term temperature perturbations, new species will come to dominate.

Previous studies have looked at the effects of high and low temperature shocks on reactor performance and on the microbial community, as well as longer-term temperature changes. For example, Bourque et al. found that when varying the temperature of a UASB reactor on a daily basis for a 6-hour interval, a 10°C increase resulted in an increase in methane production and an increased COD removal. However, methanogens were only tolerant to these temperature shocks over a short term of 2-6 hours.[31] In an experiment probing longer-term temperature variations, the temperature of a Psychrophilic anaerobic digester operating at 15°C was decreased to 5°C. This resulted in a decrease in COD removal efficiency at first, but then the performance was partially recovered, although not to full capacity.[32] The overall conclusion of the study was that a decrease to 10 °C did not significantly impact reactor performance, but a decrease to 5°C significantly decreased the COD removal efficiency and caused sludge disintegration. Other research has shown that temperature increases can be detrimental to reactor performance and sludge properties. Lau and Fang showed that both temperature increases and decreases impacted Thermophilic granules, resulting in washout, low pH, and VFA accumulation, and that an increase in temperature was more detrimental than a decrease.[33] In another study with Mesophilic sewage sludge, the experimental

temperature was decreased from 30°C to 15°C in intervals of 5°C for reactors with different HRTs. After each decrease, the temperature was held constant for 30 days. Reactors with short HRTs were more severely affected by the temperature decrease, and the microbial population was impacted at lower temperatures in all reactors.[34]

The ammonia equilibrium depends on temperature and must be taken into consideration when temperature fluctuates.[35] Free ammonia is inhibitory to methanogens, and at higher temperatures the ratio of free ammonia to total ammonium will be higher. However, the interactions between temperature and ammonia are complex. Garcia and Angenent found that elevating temperature increased methanogenesis rates significantly enough to overcome inhibition effects from ammonia.[36] However, El-Mashad found that all three steps of anaerobic digestion, including hydrolysis, acidification, and methanogenesis, were negatively affected by temperature increases, likely due to increases in ammonia concentrations at higher temperature.[37]

Influent pH

Changes in influent pH can have significant impact on reactor performance depending on the buffer capacity in the reactor.[38] Methanogenic microorganisms have optimal activity between pH 6.3-7.8. Acidogenic microorganisms are less sensitive to pH variations and acids will continue to build up as pH decreases. Borja and Banks looked at the performance of an anaerobic fluidized bed reactor in response to organic load, hydraulic load, temperature, and pH shocks. The variations were implemented for 6 and 12-hour periods, and the reactor typically recovered within 6-16 hours. It was

demonstrated that the reactor had sufficient alkalinity to handle a low pH of 3.0 and a high pH of 10.0 without negative impacts on reactor performance.[39]

Of the methanogens, acetoclastic methanogens are more sensitive to pH changes than hydrogenotrophic methanogens.[40,41] pH changes can favor one methanogenic group over the other, changing the ratio of methane to carbon dioxide in the biogas. In a study of UASB reactors treating methanolic wastewater, Bhatti et al. demonstrated that while low pH was inhibitory to acetoclastic methanogens, hydrogenotrophic methanogens remained active. At a pH of 7.0, acetoclasts were favored, while at pH 5.0-6.0 hydrogenotrophic methanogens were favored.[42]

Timing of Variations

Leitão et al. also concluded that occasional pulses or step changes in concentration or wastewater flow conditions are common in breweries and food-processing operations. These fluctuations sometimes allow enough time for operators to take proper measures, but other times the shocks are sudden and the reactors need sufficient buffer capacity to handle the changes.[43]

Stability of Reactors Treating Brewery Wastewater

There have been several studies focusing on the stability of reactors treating brewery wastewater in particular. One study compared Psychrophilic and Mesophilic digestion of brewery effluent. The lower temperature, lower capacity Psychrophilic digester gave 50% less biogas yield, but COD removal efficiencies and methane content of the biogas at maximum loading rates were the same.[44] Li and Mulligan looked at the

treatability of waste beer in two different types of anaerobic digesters, and found that at Mesophilic temperatures, treatment of waste beer was sustainable at limited organic loading rates.[45]

Other studies have looked at pilot-scale brewery wastewater treatment plants in response to varying operational and environmental conditions. Oktem and Tufekci operated a pilot-scale UASB reactor at 35°C. The reactor was operated for six months and the OLR was increased up to 10-15 kgCOD/m^3/day. It was possible to reduce the HRT to 0.5 days while still achieving a sludge bed with good settleability and activity.[46] Nagel et al. looked at the toxicity effects of several cleaning products on methanogenic microorganisms, including detergents, disinfectants, and lubricants used in brewery operations. Toxicity levels were established for each product and under pulse loading conditions, the operational behavior usually decreased until a new steady state was reached. The reactors typically adapted and recovered at the end of the shock.[47]

Despite findings reported in the literature on the stability of anaerobic digesters, the lack of research in the area of digesters treating brewery wastewater justifies further research in this area. No studies to date have investigated the typical perturbations experienced in a real brewery and studied the effects of these perturbations on the anaerobic digestion process and granule stability. In addition, a simplified model and on-line monitoring and controls program for anaerobic digesters with primarily on-line sensing capability does not exist today. Therefore, the present study is designed to determine the effect of real-world brewery operational and environmental variations on the anaerobic digestion process stability and granule stability, as well as evaluate the

potential of several on-line sensors in a monitoring and predictive controls solution for the industry.

In order to perform controlled variations to mimic real perturbations experienced in brewery wastewater treatment, experimental perturbations were planned with collaborators at Cornell University based on analysis of operational data from an actual brewery wastewater treatment plant and the advice of brewery plant operators. Several perturbations were identified as common variations that could potentially disrupt the stability of the anaerobic digestion process. These variations include low pH, temperature increases or decrease, a beer spill, a shock of bottling line lubricant (long chain fatty acids in feed), hydraulic shock, concentration shock, increase of incoming solids, and an alkaline spill (soaker dump). In addition, the recycle rate often increases, decreases, or shuts off completely, impacting the hydraulic flow and gradients in the reactor. These common brewery variations threaten upset and instability in the anaerobic digester. It is necessary to test these variations on the lab-scale and model the anaerobic digestion process to gain insight into how microorganisms in UASB reactors respond. This will provide data for a model that will predict and control the process to avoid costly shutdowns and upsets.

Monitoring Parameters

Since anaerobic digesters experience a wide variety of operational and environmental conditions, it is important to provide operators with the right controls solution to handle upsets. This will minimize negative impacts on plant operations and prevent costly shut-downs for maintenance or restarting the process. Given the complex

interactions within the anaerobic digestion process, an accurate and detailed model is required to predict and prevent upsets. The predictive monitoring and controls solution must provide insight into the health of the digester using sensing equipment that is robust and reliable in an industrial setting, easy for operators to use and interpret, and cost effective.

Vanrolleghem reviewed the different sensing technologies used to monitor the anaerobic digestion process.[48] The typical characteristics of an upset digester are decreased pH and alkalinity, increased VFAs, decreased biogas production, decrease in the methane content in the biogas, and sludge washout. In typical wastewater treatment plants, routine monitoring is limited to flow rates, gas production, and pH. Many liquid phase parameters inside the reactor, such as VFAs and alkalinity, lack efficient, robust, inexpensive online sensors.[49,50] While liquid phase parameters provide direct insight into the health of the reactor, gas-phase parameters also provide information about reactor performance and on-line sensors for gas composition and flow rates are more readily available.

The goal of this study was to use available on-line and off-line sensing technologies and to measure reactor parameters. The on-line and off-line data will be used to validate and instruct anaerobic digestion models, and the predictive monitoring and controls solution will be simplified to the key indicators of upset that must be monitored.

Alkalinity, pH, and VFAs

As discussed previously, the relationship between pH, alkalinity, and VFAs provides important information about digester operation. pH can be measured online, but pH probes are limited in sensitivity and are often subject to fouling in the conditions of the reactor. In addition, measurement and adjustment of pH alone is not enough, as sufficient alkalinity is essential for proper pH control. The pH and alkalinity depend on the chemical equilibrium inside the reactor and are affected by several different chemical species, the most important being the carbon-dioxide bicarbonate equilibrium. The equilibrium between carbon dioxide in the biogas and bicarbonates in the reactor is a function of pH (Figure 6).[51] Bicarbonate alkalinity and pH in the reactor change as anaerobic digestion proceeds. Ammonium bicarbonate alkalinity is produced as proteins are degraded and ammonia and carbon dioxide are released, and bicarbonate alkalinity is destroyed when volatile fatty acids are neutralized. Bicarbonate alkalinity can be a much earlier indicator of upset than pH and a great deal of information can be gained from measuring the pH and alkalinity in the anaerobic digester. For example, Hawkes et al. monitored bicarbonate alkalinity during organic overloads and found that bicarbonate was a good indicator of instability and overload. In addition, alkalinity measurements taken together with carbon dioxide concentration in the biogas provided a reliable estimate of reactor pH.[52]

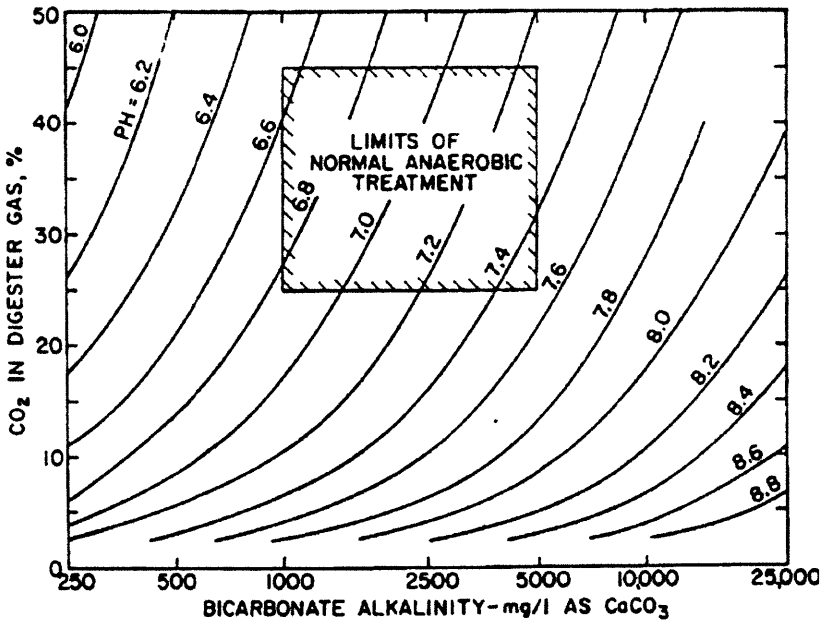

Figure 6. Limits of anaerobic treatment. Figure reprinted from McCarty, Perry. Anaerobic Waste Treatment Fundamentals. Public Works, 1964, No. 9, 10, 11, 12, Page 125 with permission from Perry McCarty.

VFAs are an important intermediate in the anaerobic digestion process. The build-up of organic acids is an early signal that the production of methane is inhibited and that VFA production has exceeded the capacity of methanogens to metabolize acetic acid. For example, Nielsen et al. looked at methane production and propionate concentration as indicators of upset and found that increased propionate concentration was an early warning of upset. Changes in propionate concentration over time were also representative of the overall system's return to stable operation.[53] Ahring et al. also demonstrated a significant change in VFAs within 2 days of overloading, and VFAs remained high for several days even after methane yield in the biogas returned to normal.[54]

Gas Composition

Composition of the biogas, particularly the ratio of methane to carbon dioxide, is another useful parameter for monitoring stability of the anaerobic digestion process. An increase in the carbon dioxide percentage in the biogas indicates that methanogens may be inhibited. In addition, the combination of pH and carbon dioxide in the biogas can provide information about the bicarbonate alkalinity in the reactor liquid.

Hydrogen in the biogas is another potential indicator of upset. There is a narrow thermodynamic window where anaerobic digestion reactions will proceed (Figure 7). The conversion of higher VFAs like propionate and butyrate to acetic acid and hydrogen have positive free energies, and a low partial pressure of hydrogen is necessary for these reactions to proceed. Therefore, a stable process depends on the close interaction between hydrogen producers and hydrogen consumers. Methanogens typically use any hydrogen present in the digester liquid very quickly to maintain a low partial pressure, so any increase in hydrogen in the reactor is an indicator that methanogens are inhibited and that acid-formers and acid-consumers are out of balance. Hydrogen has been investigated as a monitoring parameter in anaerobic digesters and has proven to be an early indicator of upset. For example, Guwy et al. looked at hydrogen concentration in the biogas while increasing OLR, and observed significant increases in biogas hydrogen concentration up to 1450 ppm.[55] Huang et al. observed a 140% increase in hydrogen concentration within an hour of organic shock loads.[56]

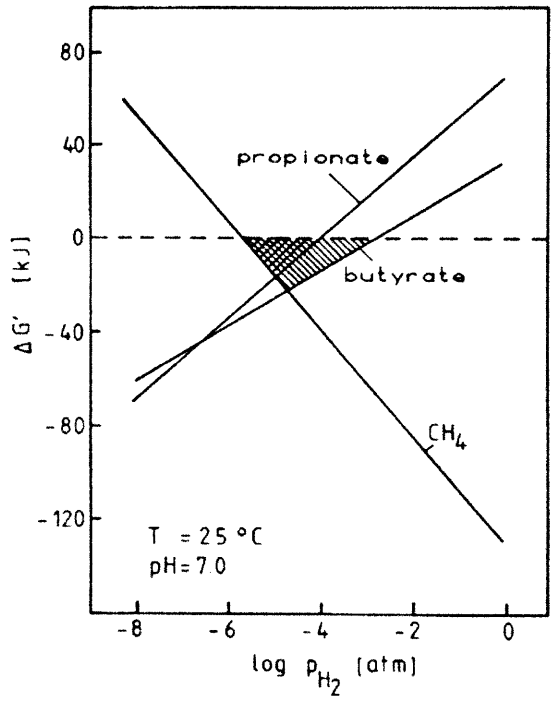

Figure 7. Narrow thermodynamic window for anaerobic digestion to proceed. Figure reprinted from Technology Transfer in Biotechnology, Volume 92, 2005, Page 55, Biochemical Reaction Engineering and Process Development in Anaerobic Wastewater Treatment from Advances in Biochemical Engineering/Biotechnology Series, Alexander Aivasidis and Vasileios I. Diamantis, Figure 4 Copyright 2005 Springer Berlin/Heidelberg with kind permission of Springer Science+Business Media.

Summary of Parameters

It is difficult to gain insight into the health of the digester from just one of these variables, but several parameters taken together can indicate whether a digester is operating efficiently. This project proposes to explore different monitoring parameters under varying process conditions. From these parameters, a predictive model will be developed, with specific indicators of upset to be monitored, and controls solutions in response to these upsets will be established. The goal is to create a simple model that incorporates the key parameters, focusing on parameters that can be monitored on-line to

give the most accurate, real-time information about reactor performance, and to decrease the time and skill necessary for operators to respond to conditions likely to upset. The experiments will also measure some variables off-line, to see if the on-line data can be used to accurately infer these off-line variables.

Materials and Methods

Experimental Set-Up

Two glass UASB reactors were constructed by the Mid-Rivers Glassblowing company using a design developed by academic collaborator Lars Angenent. The reactors had a working volume of 5.0 L and a height of 76 cm, and consisted of an inner reactor vessel (diameter 8 cm) surrounded by a glass heating jacket (diameter 10 cm). Water was circulated into the heating jacket using a heating bath (Neslab RTE-211) to maintain the reactor temperature at 37°C. Each reactor had an inlet port at the bottom and two sampling ports along the length of the reactor, approximately 15 cm and 66 cm from the reactor bottom. Marbles in the bottom of the reactor served as a feed distribution system at the reactor inlet. The upper section of the vessel was approximately 38 cm in height and 13 cm in diameter, with a recycle port and an effluent port for fluid overflow. An inverted cone in the top portion served as a gas-liquid separation system, with an inverted funnel to prevent biomass washout and to collect biogas. The stem extended through the reactor headspace and directly connected to the gas line. Steel tubing was used to connect to the hydrogen sensor to minimize the diffusion of hydrogen from the biogas, and Viton tubing was used for the carbon dioxide and methane sensors to reduce diffusive losses through the tubing wall. (Figure 8, Figure 9)

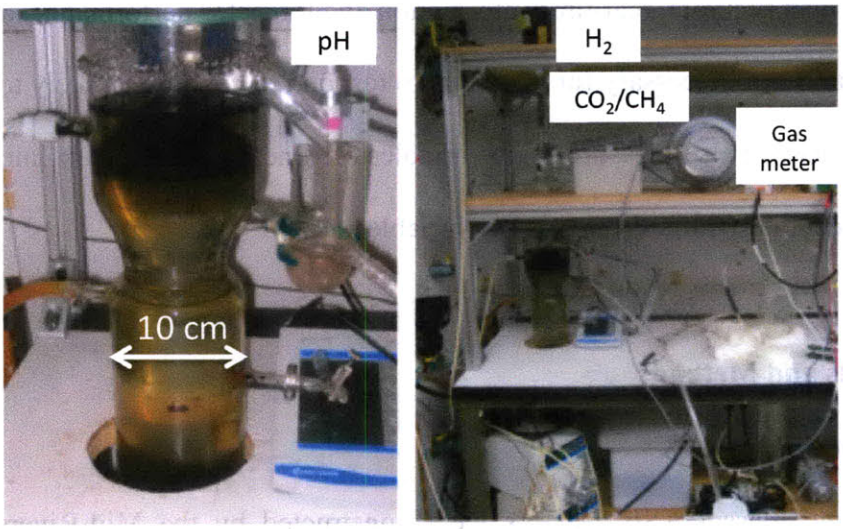

Figure 8. Photos of reactor set up

Influent

A sample from the wastewater flowing from a pre-acidification reactor into a UASB reactor at a brewery wastewater treatment plant was collected and analyzed by collaborator Dr. Lars Angenent to determine the typical properties of brewery wastewater (Table 1). The synthetic feed in this study was prepared to closely mimic the wastewater properties of this brewery and was composed of glacial acetic acid (Sigma), glacial propionic acid (Sigma), beer (Anheuser Busch Budweiser), yeast extract (Difco), trace elements solution, NH_4Cl (Fisher), K_2HPO_4 (Aldrich), and $MgSO_4$ (Sigma) (Table 2). The amounts of acetic acid, propionic acid, and beer were added to provide an influent soluble chemical oxygen demand (SCOD) of 1500 mg/L, with 85% of the SCOD coming from volatile acids and the remaining 15% form ethanol and carbohydrates in beer. The feed was supplemented with NH_4Cl and K_2HPO_4 to achieve the recommended COD:N:P ratio of 400:7:1 for biomass growth.[57,58] This ratio is based on the approximate COD

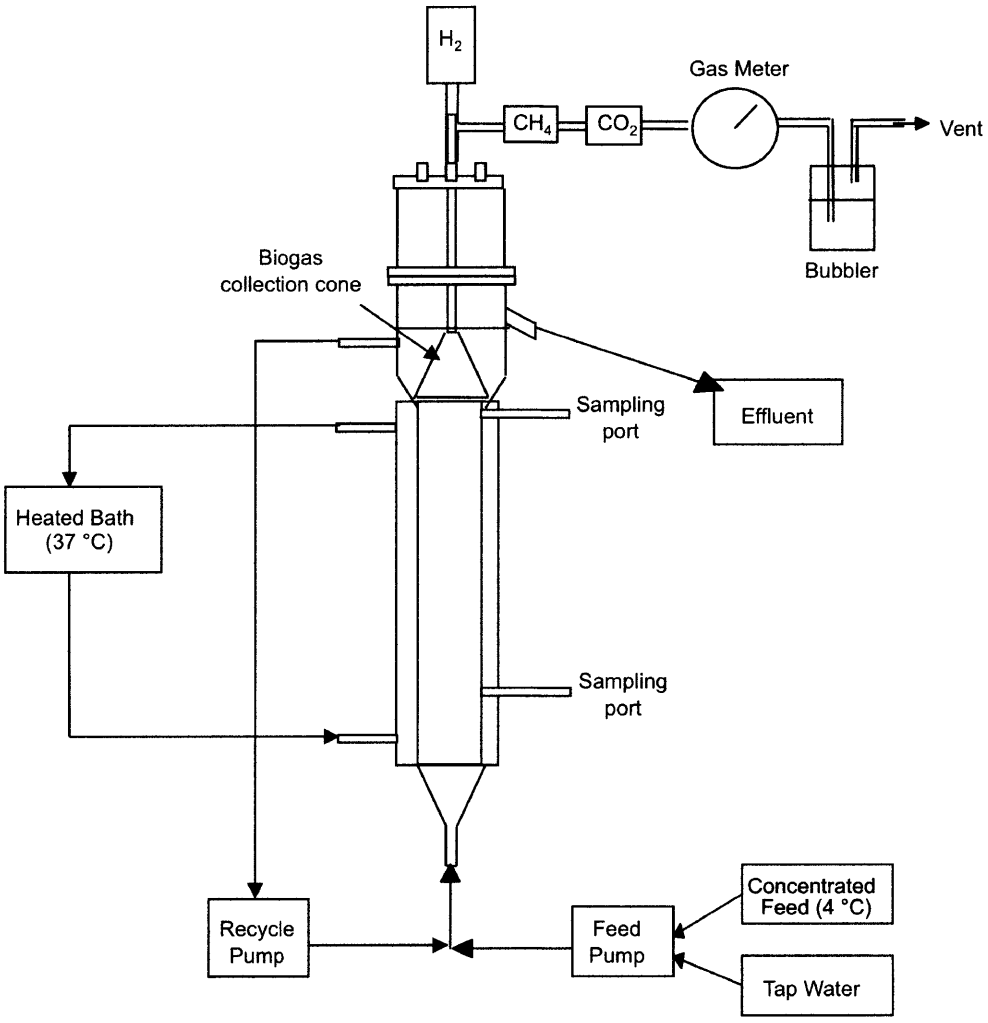

Figure 9. Reactor diagram

Table 1. Characteristics of wastewater entering UASB reactors from a pre-acidification tank

Property	Measurement
pH	5.95
Ammonium	1.17 mM
Total Alkalinity	380 mg/L
Total Solids	2850 mg/L
Total Suspended Solids	1530 mg/L
Volatile Suspended Solids	1050 mg/L
Fixed Solids	480 mg/L
Total COD	2811 mg/L
Soluble COD	1378 mg/L
Acetate	4.9 mM
Propionate	5.2 mM
Isobutyrate	None Detected
Butyrate	0.6 mM
Isovalerate	0.3 mM
Valerate	0.6 mM

Table 2. Components in synthetic feed

Concentrated Feed	
Component	**Amount in mL or g per 9 L Concentrate**
Beer	396 mL
Glacial acetic acid	90 mL
Glacial propionic acid	70.2 mL
Trace elements stock solution	180 mL
Yeast extract	18 g
NH_4Cl	18 g
K_2HPO4	2.97 g
$MgSO_4$	2.934 g

loading and reactor efficiency, assuming that approximately 15% of SCOD treated will be converted to new biomass and that the approximate makeup of a bacteria cell is $C_5H_7O_2N$.[59]

The trace elements solution composition was based on the recipe from Zehnder et al. (Table 3).[60] To prepare the trace elements stock solution, each of the components were added to 1 liter of tap water in a 0.5 gallon glass bottle equipped with a stir bar. Then the stock solution was diluted with water to a final volume of 1 liter and allowed to stir overnight. The solution was stored at room temperature.

Table 3. Trace element stock solution

Trace element stock solution	
Component	**Amount [mg/L]**
$FeCl_2*H_20$	2,000
$MnCl_2*4H_2O$	500
$CoCl_2*6H_20$	2000
$NiCl_2*6H_20$	142
$ZnCl_2$	50
Na_2SeO_3	123
$AlCl_3*6H_20$	90
$(NH4)_6Mo_7O_{24}*H_20$	50
$CuCl_2*2H_20$	38
Resazurin dye	200
H_3BO_3	50
HCl	1 mL/L 36%
EDTA	1000

A concentrated feed was prepared every 7 days and stored at 4 °C. To prepare the feed, acetic acid and propionic acid were added to 4 liters of tap water in a 9 liter container equipped with a stir bar. The pH was adjusted to 5.1 using 50 %w/w NaOH

(Fisher) and a benchtop pH meter and electrode (Accumet AB15). Then the beer, trace elements solution, yeast extract, NH_4Cl, K_2HPO_4, and $MgSO_4$ were added to the solution. The feed solution was then diluted to a final volume of 9 liters and stored and continuously mixed in a refrigerator at 4 °C.

The concentrated feed was diluted 10:1 with tap water and fed to the reactor. Norprene tubing was used for all feed lines and Masteflex Standard L/S pump heads were used for all pumps. Each reactor had two pumps controlling the influent: one pump for the recycle (Masterflex L/S Computerized Pump Drive, 1-100 RPM) and one pump with two pump heads for the tap water and concentrate (Masterflex L/S Computerized Pump Drive, 6-600 RPM) which maintained a constant dilution ratio. The reactors were equipped with size 14 tubing for the concentrate and size 24 tubing for the tap water, and the two lines were combined into a single size 16 tubing line. Then this feed line was combined with the recycle line into a single line feeding into the reactor inlet. The baseline flow rate of the concentrate was 0.9 mL/min, and the baseline tap water flow rate was 9 mL/min, giving a dilution ratio of 10:1 and a baseline feed flow rate of 10 mL/min.

Start-Up and Continuous Operation

The reactors were inoculated with 2.5 L of granular biomass taken from the Anheuser-Busch Brewery Wastewater Treatment Facility in Baldwinsville, NY. Prior to inoculation the biomass was stored at 4 °C. The recycle:feed ratio and upflow velocity were determined based on the conditions experienced in full-scale brewery wastewater treatment. During the start up process, the recycle ratio was gradually increased to a ratio

of recycle:feed of 6:1 in order to achieve partial fluidization of the biomass bed. The hydraulic retention time for the reactor under these conditions was 8.4 hours, and the linear upflow velocity was 0.64 m/h.

Analysis

Table 4 details the sampling schedule, analytical techniques, and instrumentation used to monitor the health of the UASB reactors. All on-line data was collected using a Dataq 710 A/D converter. CO_2 and CH_4 concentrations in the biogas were measured using Gascard dual-wavelength infrared gas sensors (Edinburgh Instruments). Different gases will have strong absorption at different infrared wavelengths based on particular frequency of vibration of their interatomic bonds. Methane absorbs around 3.4 microns, and carbon dioxide absorbs around 4.26 microns. The Gascard II models had a measurement range 0-100% CO_2 and 0-100% CH_4 with an accuracy of +/- 2% of the range. The sensors were calibrated for a biogas background using five gas standards: 100% CH_4; 100% CO_2; 25 % CO_2, 75% CH_4, 0.01% H_2; 34% CO_2, 66% CH_4, 0.025% H_2; and 50% CO_2, 50% CH_4, 0.05% H_2 (Scott Specialty Gases).

Hydrogen concentration in the biogas was measured using the HY-OPTIMA 740 In-Line Process Hydrogen Monitor (H2Scan). The sensor operation is based on the interaction between a palladium-nickel thin film and hydrogen gas molecules. H_2 molecules present in the gas stream will interact with the thin film and dissociate into atomic hydrogen. The atomic hydrogen diffuses through the thin film, changing the

Table 4. Monitoring schedule, analytical techniques, and instrumentation of UASB reactors

Monitoring Schedule, Analytical Techniques, and Instrumentation					
		Sampling Frequency			
Parameter	**Sampling Location**	Steady state	During process upset	**Technique**	**Instrument**
Ambient Temperature and Pressure	Inside hood	Continuous	Continuous	Temperature probe, barometer	R.M. Young Model 41342VC RTD temperature probe, Vaisala PTB110 barometer
pH	Influent, reactor sampling ports, effluent	Continuous	Continuous	pH probe	Mettler Toledo long-stem probe, Omega Microprocessor-based pH controller with automatic temperature compensation
Fluid flow	Influent, effluent	Continuous	Continuous	Pump calibration	Masterflex L/S Pump Drives, Masterflex L/S Computerized Pump Drives
Gas flow	Gas line	Continuous	Continuous	Gas meters	Actaris Laboratory Meter
Gas composition	Gas line	Continuous	Continuous	CH_4, CO_2- IR sensors, H_2Scan sensor	Edinburgh Instruments Gascard II, H2Scan Hy-Optima 740
COD	Influent, effluent	3 times per week	Daily	Standard Methods 5220D. Closed Reflux, Colorimetric Method	Hach COD analysis unit and digestion vials, Cole Parmer 0.45 micron PTFE Nonsterile Syringe Filters
Alkalinity	Influent, effluent	3 times per week	Daily	Standard Methods 2320B	Thermo Scientific Ross pH electrode (combination, general purpose, glass body), Hamilton Syringe (1000 Series Gastight, PTFE Luer Lock, volume 5.0 mL), Cole-Parmer single-syringe infusion pump
Individual VFAs	Influent, effluent	3 times per week	Daily	Gas Chromatography	Agilent HP 5890 Series II, Supelco Nukol Column 0.53 mm x 30 m

resistivity of the Pd/Ni alloy. The resistivity is correlated to a particular hydrogen concentration in the gas.[61,62] This sensor was operable in an anaerobic environment and had a coating to protect the sensor from background gases of carbon monoxide, water vapor, methane, and hydrogen sulfide, which may also be present in the biogas stream. H2Scan specifically calibrated the sensor for this application to be sensitive in lower

concentration ranges of 1-1000 ppm H_2, with a limit of detection of 15 ppm. The hydrogen sensor was calibrated prior to perturbations, as any oxygen present on the surface of the sensor will interfere with hydrogen adsorption to the thin film.

Gas flow rates for the reactors were measured continuously using a High Accuracy Wet Test Laboratory Gas Meter (Actaris Metering Systems). Ambient temperature and pressure were also measured continuously to adjust gas volumes to STP (R.M. Young Model 41342VC RTD temperature probe, Vaisala PTB110 barometer). The pH in the reactor top portion was measured using a long-stem pH electrode (Mettler Toledo) and a digital pH panel meter (Omega PHCN-37-AI). Temperature in the reactors was measured using a thermocouple (Cole Parmer Digisense K-Type Thermocouple Thermometer). The temperature probe was inserted into the reactor and the temperature was measured approximately 30 cm from the bottom of the reactor. The difference in temperature between the heating bath setting and the reactor temperature was measured initially to establish a correction factor for reactor temperature.

Total and soluble chemical oxygen demand (TCOD and SCOD) were measured according to Standard Methods (Standard Methods 5220D Closed Reflux, Colorimetric Method) using a COD analysis unit (Hach DRB 200) and COD digestion vials (Hach High Range 20 to 1500 mg/L Digestion Vials). Samples were collected from the reactor influent and the effluent, and for SCOD, samples were filtered with 32 mm 0.45 micron PTFE syringe filters (Cole Parmer). Then 2 mL of the sample was injected into the digestion vial and the samples were heated to 150°C for two hours, during which time organics present in the sample will react with potassium dichromate in the digestion vials. Potassium dichromate is an oxidizing agent, so it will oxidize organic compounds in the

sample to carbon dioxide and water. When potassium dichromate is reduced, the dichromate ion is reduced to green chromic ion. The amount of chromic ion produced is determined by a colorimeter, and this is correlated to the amount of oxidant required to oxidize the sample completely. The color change was then measured with a colorimeter (LaMotte 2 Colorimeter, COD Standard Range Test) and the results are reported as mg of oxygen per liter of sample.[63] Standards were measured weekly using a 1000 mg/L COD standard solution (Hach), and the limit of detection was 3mg/L. For batch analysis, samples were stored at 4°C and 20 uL of concentrated sulfuric acid (Fisher) was added to preserve the samples for subsequent analysis.

Individual volatile fatty acid concentrations were measured by gas chromatography with a flame ionization detector (Agilent HP 5890 Series II) and a Nukol Bonded Free Fatty Acid Phase column (30 m L x 0.53 mm ID, Supelco). Samples were collected from the reactor influent and effluent, filtered with a 0.45 micron PTFE syringe filter (Cole Parmer 32 mm diameter), diluted 1:1 with 2% formic acid to acidify (Fisher), and then stored at 4 °C for one week until batch analysis. The samples were then injected by an autosampler (HP 7673 Injector). The FID detector was run with an Air:H_2 ratio of 10:1, with an H_2 flow rate of 35 mL/min, an air flow rate of 350 mL/min, and a helium flow rate of 10 mL/min from the column. The temperatures of the injector and detector were 230 °C. The column temperature was held at 85°C for two minutes and then the temperature was increased at a rate of 20 °C/min up to 200°C. The temperature was then held at 200°C for two minutes. Two injections of 2% formic acid were injected in between each sample to remove any residual peaks from the column.[64] Standards were

prepared weekly with 5 different concentrations prepared from 10 mM volatile acid standard solution (Supelco). Results were analyzed using Agilent ChemStation software.

Alkalinity was measured based on the Standard Methods (Standard Methods 2320B) using a pH electrode (Thermo Scientific Ross pH electrode), Hamilton Syringe (1000 Series Gastight, PTFE Luer Lock, volume 5.0 mL), and a syringe pump (Cole-Parmer single-syringe infusion pump). 10 mL of sample were collected in a 50 mL beaker and placed on a stir plate with gentle stirring. The pH probe was then placed into the sample and 0.1 N sulfuric acid (Fisher) was added to titrate the sample to pH 4.3. The volume of sulfuric acid used was recorded and then alkalinity is calculated in mg/L as $CaCO_3$ based on the volume of acid used, the acid normality, and the volume of sample.

Experimental Plan for Perturbations

The controlled variations were divided between the reactors at Cornell at GE (Table 5). Both labs established equilibrium conditions in the two reactors before performing perturbations. Both labs also performed the first low pH perturbation to ensure reactors were operating similarly between sites. In the future, the labs will split up the perturbations, returning to steady state in between each perturbation.

Results

Start-Up and Continuous Operation

One reactor was continuously fed with synthetic brewery wastewater at an initial OLR of 7.4 gCOD/L/day. Over the first 20 days of operation, the recycle rate was

Table 5. Experimental plan for controlled perturbations at GE and Cornell

Cornell	GE
0. Establish equilibrium at new influent pH	0. Establish equilibrium at new influent pH
1. Low pH	1. Low pH
2. Wort spill	2. Temperature (low and high)
3. Line lubricant	3. Hydraulic shock (same concentration)
4. Incoming solids	4. Concentration shock
5. "Soaker dump" alkaline spill	5. "Soaker dump" alkaline spill

gradually increased to a 6:1 recycle:feed ratio, giving a linear upflow velocity of 0.64 m/h. After 22 days of operation, the pH of the feed was decreased in order to more closely match the conditions of a full-scale brewery. After 69 days, the feed concentration (COD) was increased by 26% and the reactor continued to run at a new OLR of 9.4 gCOD/L/day for the remainder of the experimental period.

Reactor performance was evaluated based on gas production, gas composition, COD removal efficiency, VFA removal efficiency, and reactor pH (Figures 10-14). From the start of operation, the reactor had a very high biogas production rate that was approximately 90% of the theoretical maximum yield calculated based on COD balance (Figure 10). On Day 6 and Day 39, the continuous feed to the reactor was temporarily interrupted when the feed line was blocked. Consequently, the biogas production rate decreased severely during these times, to 3 L/day on Day 6 and 11 L/day on Day 39. On Day 6 methane decreased from 90% to 70%, while carbon dioxide decreased from 11% to 5% (Figure 11). On Day 39, which was not such a severe interruption, the

concentration of methane decreased from 83% to 79%, and carbon dioxide decreased from 7% to 6%. Upon restoring feed to the reactor, the biogas production and composition returned to steady state. On Days 14-16 the experimental period the reactor was inadvertently fed a feed with a higher concentration of sulfate. This resulted in a decrease in biogas production from 14 L/day to 12 L/day because the increased sulfate in the feed promoted the growth and activity of sulfate-reducing bacteria, thereby inhibiting methanogens. In addition to decreased biogas production, methane in the biogas decreased from 90% to 86% and the carbon dioxide decreased from 8% to 5%. Toward the end of the experimental period on Day 75, the CO_2 and CH_4 sensors were recalibrated, with new steady state values of 82% CH_4 and 18% CO_2. After recalibration the standard deviations for the carbon dioxide and methane volume percentages were less than 1% during steady-state operation. The standard deviation for the gas flowrate meter was 1 L/day during steady-state operation.

On Day 22 the pH of the feed was lowered to better mimic actual brewery wastewater treatment conditions. While biogas production remained steady, a new steady-state gas composition was achieved as the methane concentration decreased from 90% to 83% and carbon dioxide increased from 6% to 11%. The increase in CO_2 is due to a shift in the equilibrium between bicarbonate and dissolved CO_2 (and thus the gas phase CO_2) at low pH. The increased CO_2 in turn leads to a slightly increased conversion of H_2 in the hydrogenotrophic methanogenesis reaction. The pH inside the reactor top portion was measured starting on Day 42, and was on average 7.0 during regular operation, with a standard deviation of 0.03 units (Figure 12).

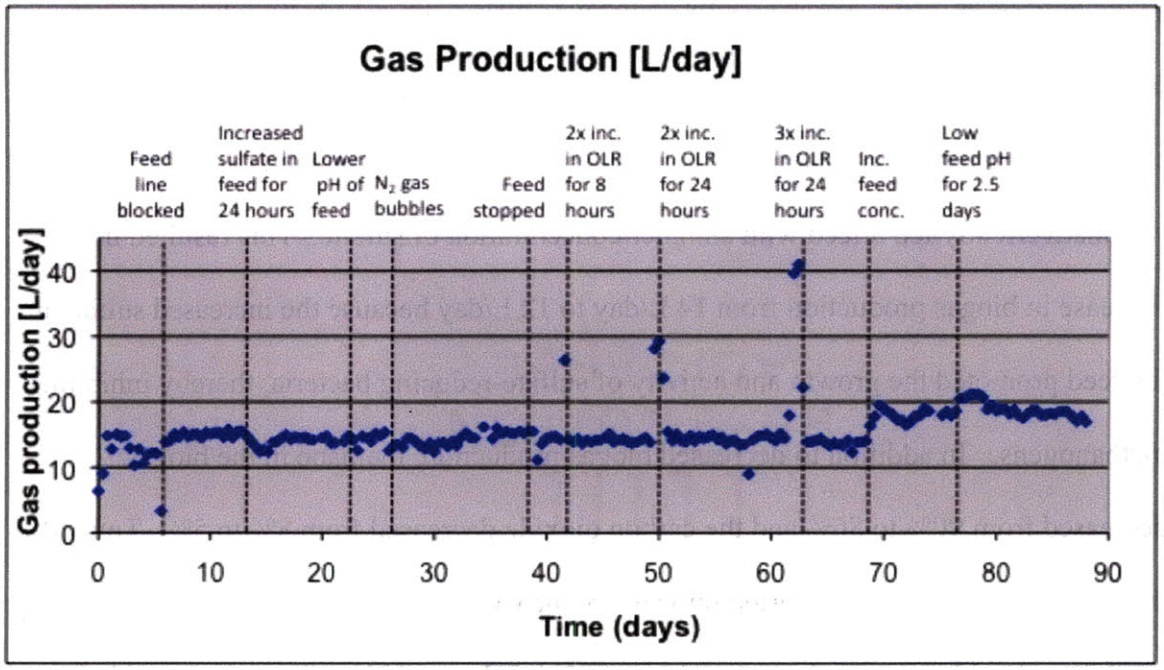

Figure 10. Evolution of gas production over the experimental period.

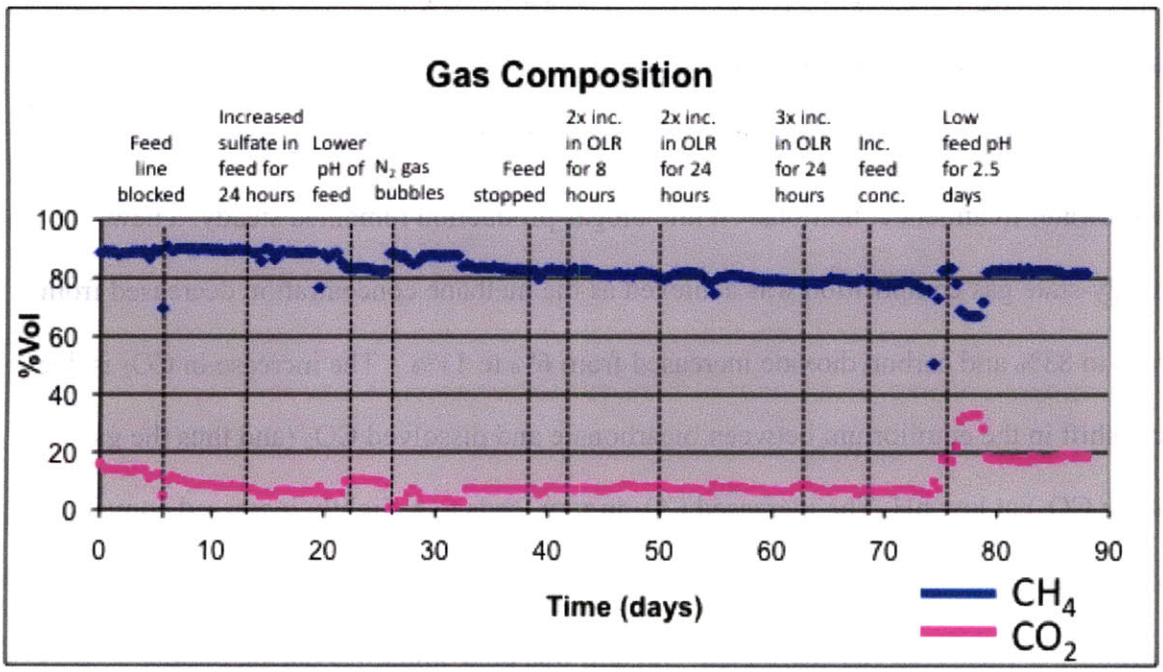

Figure 11. Evolution of gas composition over the experimental period.

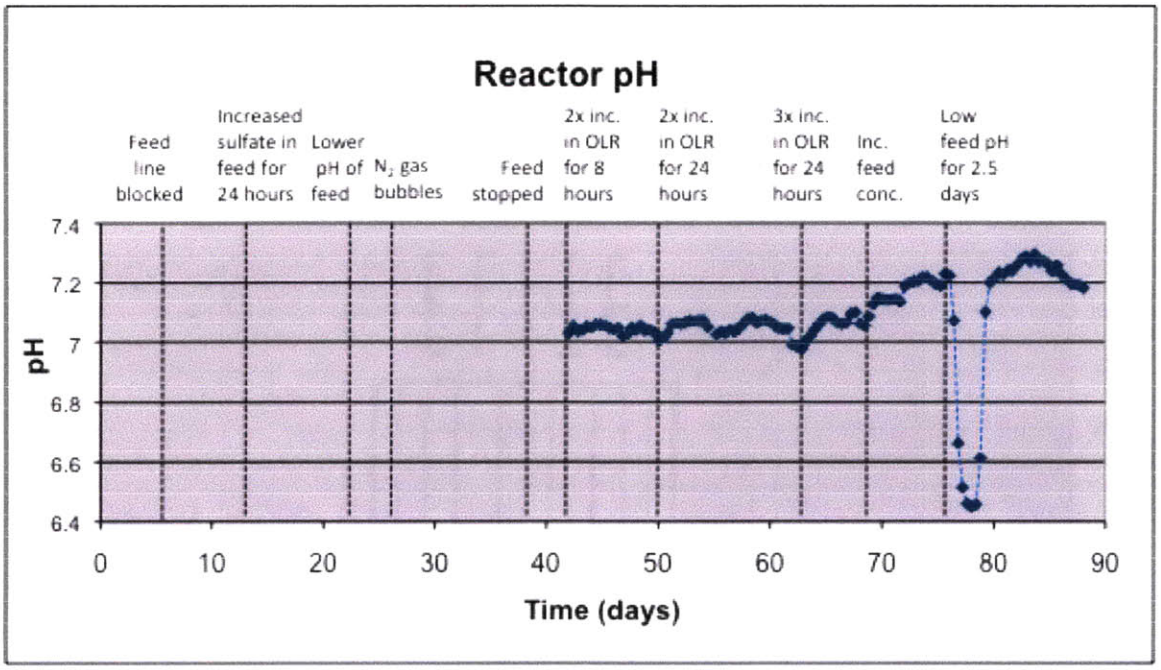

Figure 12. Evolution of reactor pH over the experimental period.

On Day 69, the concentration (COD) of the feed was increased by 26%. Consequently, the biogas production increased by 25% from 14 L/day to 17.5 L/day. This change did not affect the composition of the biogas or the SCOD or VFA removal efficiencies, but the reactor pH did increase from pH 7.0 to pH 7.2. Throughout the experimental period, even during controlled perturbations, the SCOD and VFA removal efficiencies of the reactor remained very high. The SCOD removal efficiency was consistently above 96% (Figure 13), and there were little or no VFAs present in the effluent over the course of the study (Figure 14).

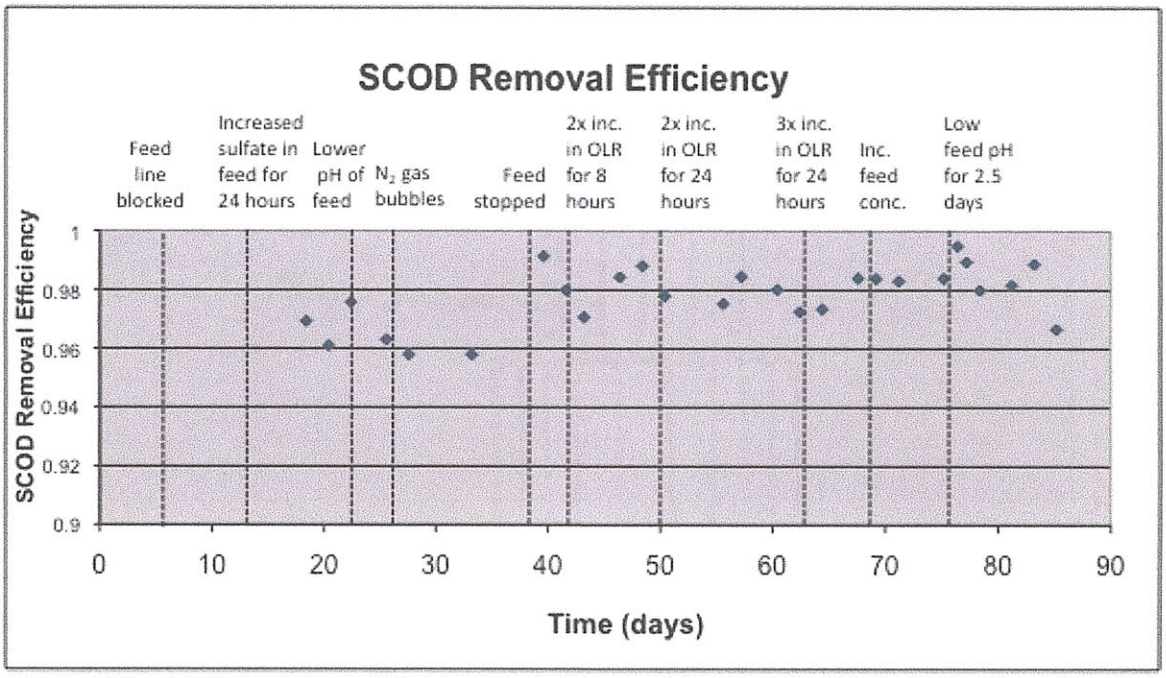

Figure 13. SCOD removal efficiency over the experimental period.

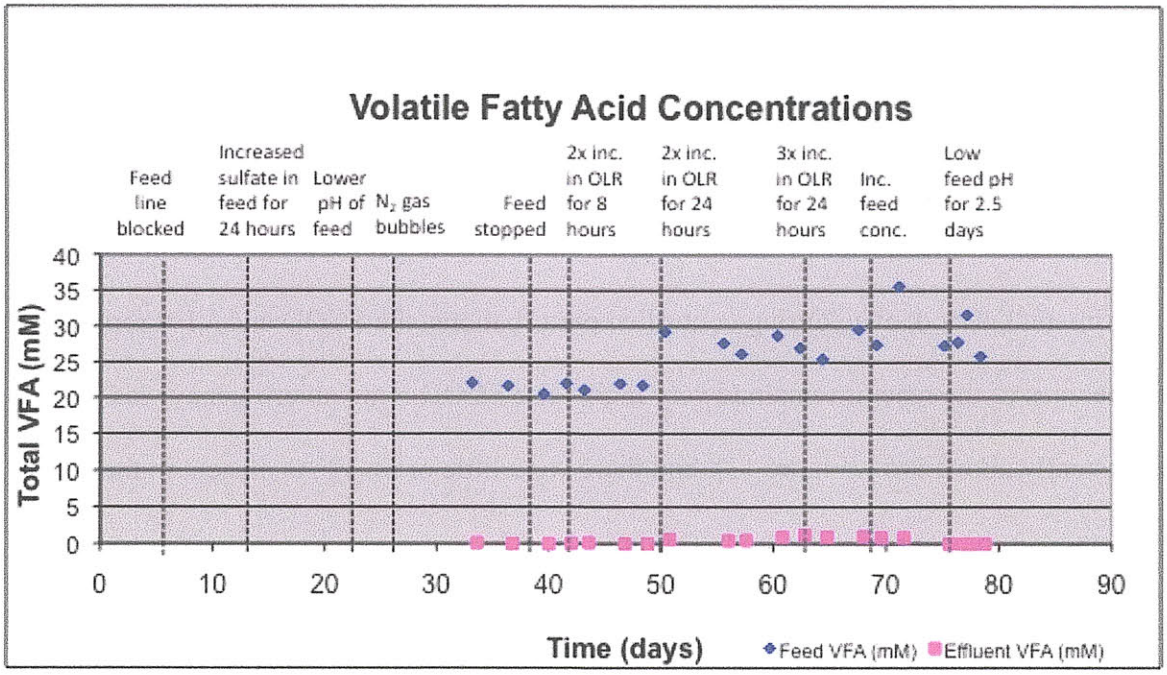

Figure 14. VFA concentrations in the influent and effluent over the experimental period.

During start up, the formation of large gas bubbles was observed, in contrast to a smooth evolution of small gas bubbles. Bubbles of biogas formed in the lower portion of the reactor coalesced to form a large bubble that lifted the entire sludge bed as it rose through the reactor. This "rising bed" phenomenon was likely due to the low linear upflow velocity in the reactor as well as the small reactor inner-diameter. (Figure 15)

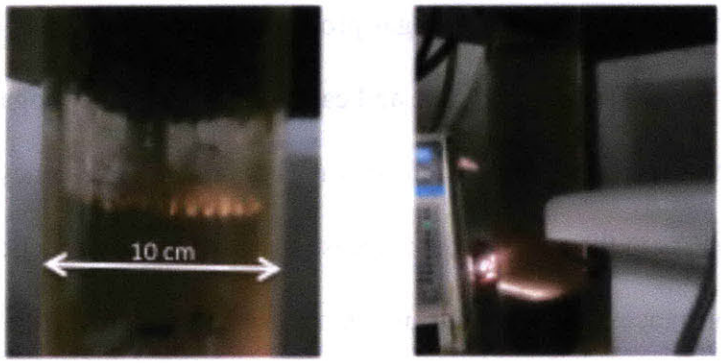

Figure 15. Rising Bed phenomenon observed during start-up.

As a temporary solution, a Teflon tube was inserted into the bottom of the reactor in order to provide a hydrophobic surface for gas bubbles to move through the reactor body. Eventually the problem was resolved after removing some biomass from the reactor, increasing the recycle ratio to 6:1, and increasing the organic concentration of the influent.

Controlled Perturbations

Increasing Organic Loading Rate

On Day 42 the organic loading rate was doubled from 7.4 gCOD/L/day to 14.8 gCOD/L/day for 8 hours, while maintaining the same linear upflow velocity of 0.64 m/h. During this time, the gas production nearly doubled, increasing from 14 L/day to 26

L/day. Methane and carbon dioxide fractions in the biogas and pH in the reactor remained constant during the perturbation, indicating that the biomass could easily handle the increase in OLR.

On Day 50, The OLR was doubled from 7.4 gCOD/L/day to 14.8 gCOD/L/day for a 24 hour time period to investigate the effects of a longer perturbation on the stability of the digester. During this perturbation, the gas production doubled to 28 L/day within 12 hours. pH inside the reactor and methane and carbon dioxide in the biogas remained constant. No effect on SCOD removal efficiency or VFA removal efficiency was observed, although VFAs in the effluent did increase to 30-40 mg/L as acetic acid.

Reactor performance was stable during the previous variations, so on Day 62 the OLR was tripled to 22.2 gCOD/L/day for 24 hours to see if a more drastic increase in feed would upset the system. During the first 12 hours the gas production almost tripled, reaching 40 L/day (Figure 16). As in the previous OLR perturbations, gas composition, reactor pH, SCOD removal efficiency, and VFA removal efficiency remained constant. VFAs in the effluent did increase slightly to approximately 50-70 mg/L as acetic acid, but this concentration was not enough to affect the balance of the anaerobic digestion process. 3 days after the perturbation, VFAs in the effluent had returned to approximately 50 mg/L as acetic acid. Carbon dioxide gradually increased approximately 2 % over the 24 hour period, but methane remained steady around 80%, indicating that methanogenesis was not inhibited (Figure 17, Figure 18). Hydrogen in the biogas also decreased to a low of 50 ppm following the start of the perturbation, but the concentration returned to 125 ppm after 14 hours (Figure 19).

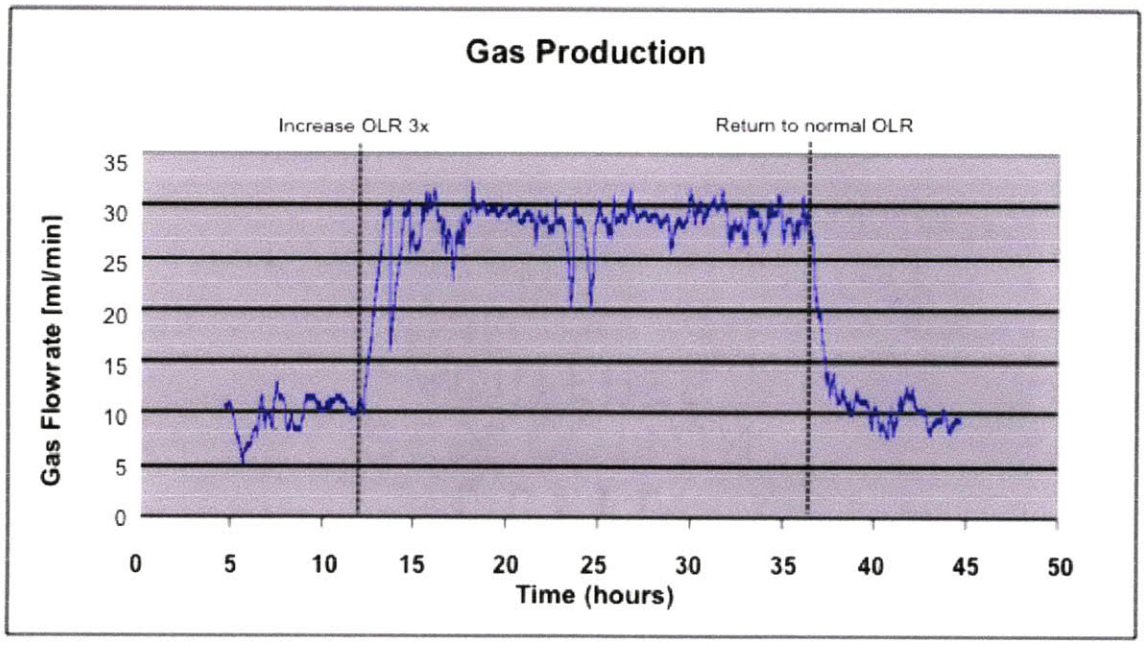

Figure 16. Gas production during 3X OLR increase for 24 hours.

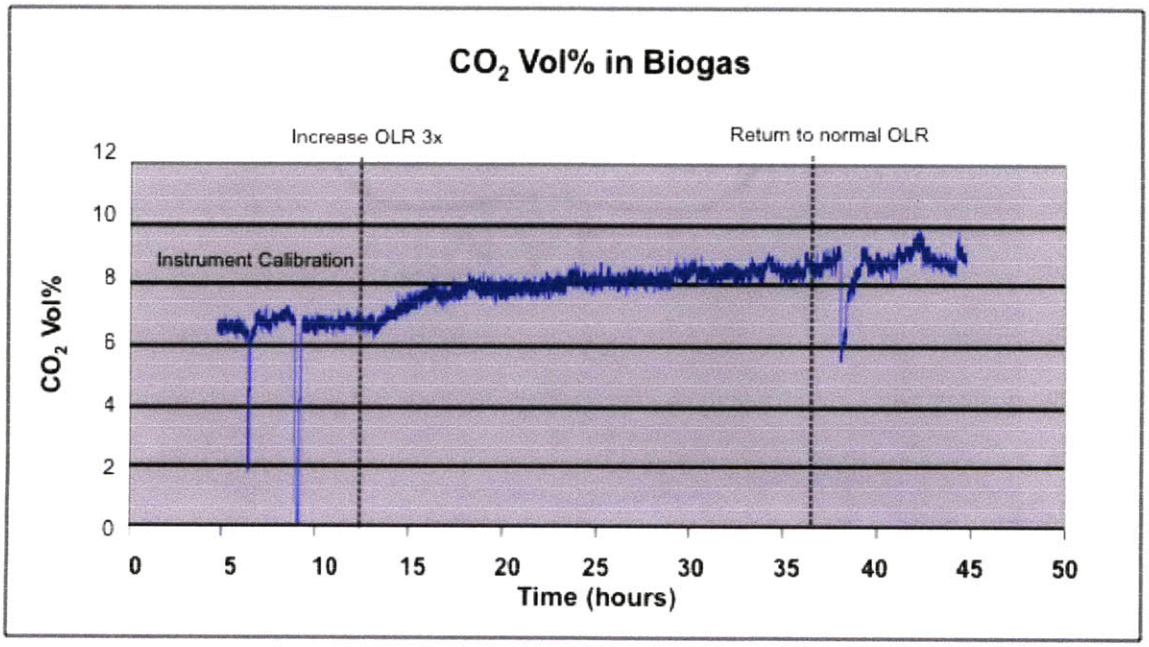

Figure 17. Carbon dioxide volume fraction in biogas during 3X OLR increase for 24 hours.

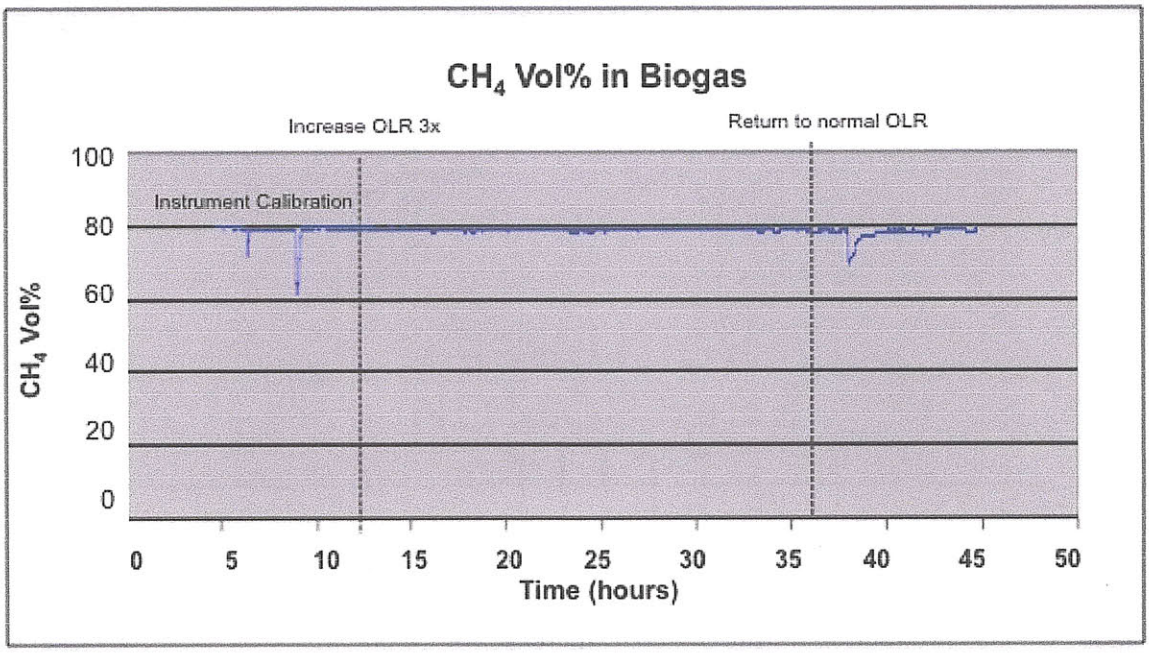

Figure 18. Methane volume fraction in biogas during 3X OLR increase for 24 hours.

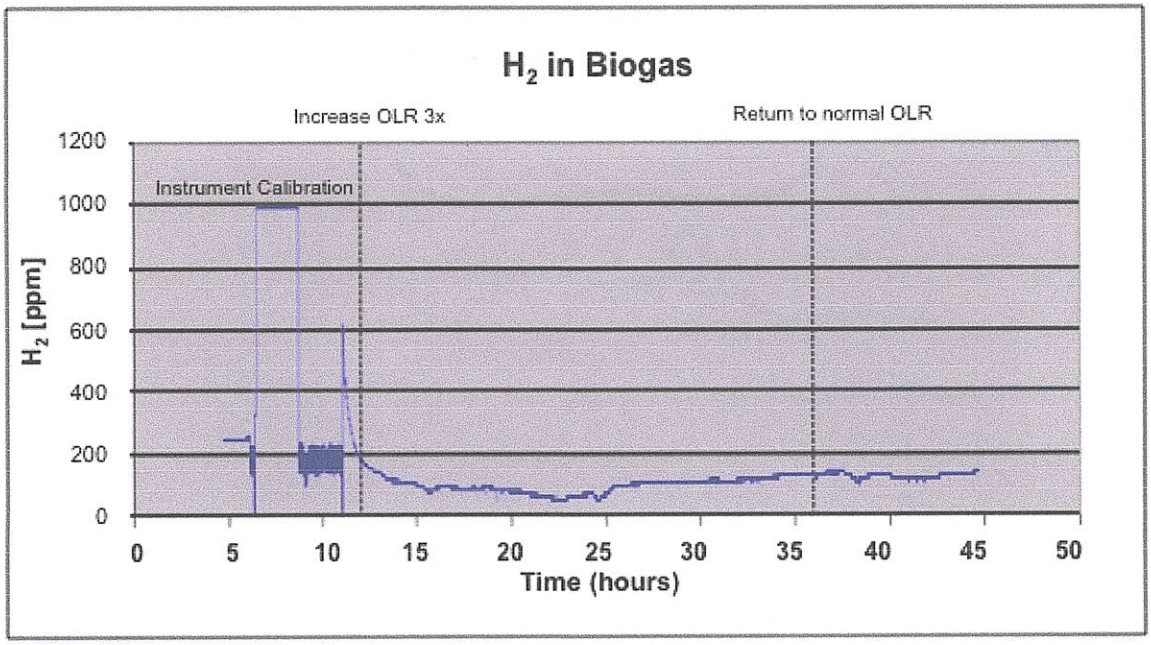

Figure 19. Hydrogen concentration in biogas during 3X OLR increase for 24 hours.

Low pH

On Day 76, the pH of the feed concentrate was decreased from 5.2 to 3.8 for 2.5 days. Gas production increased from 17.5 L/day to 20 L/day over the first 6 hours (Figure 20). Gas production remained at 20 L for the duration of the perturbation and returned to steady state value 6 hours after the end of the perturbation. Despite the low pH feed to the reactor, the SCOD removal efficiency remained high during the perturbation period (97% - 99%) and VFAs in the effluent remained low.

Carbon dioxide in the biogas increased rapidly during the first six hours from 17% to 30% (Figure 21). The carbon dioxide continued to increase and reached a new steady-state of 33% after 18 hours. Methane in the biogas also rapidly decreased initially from 83% to 70% in the first 6 hours, and eventually reached a new steady-state value of 67% 18 hours after the start of the perturbation (Figure 22). Methane production remained constant while the amount of CO_2 produced increased. This increase in CO_2 concentration is consistent with the shift in CO_2-bicarbonate balance at reduced pH. After the end of the perturbation, both methane and carbon dioxide returned to their original steady-state values within 6 hours. During the course of the perturbation, the hydrogen concentration in the biogas hydrogen concentration decreased rapidly from 325 ppm to 250 ppm over the 2 hours following the start of the perturbation and eventually reached a new steady-state value of 150 ppm after 24 hours. (Figure 23). At the end of the perturbation, the hydrogen concentration increased rapidly from 150 ppm to 200 ppm and gradually returned to steady-state over the next 24 hours.

In the low pH experiment, methane concentration decreased but the total methane production remained constant, implying that both acetoclastic and hydrogenotrophic

methanogenesis were still active. At the reduced pH, the balance in bicarbonate and CO_2 shifts towards increased CO_2, and thus a higher CO_2 concentration and a lower CH_4 concentration in the gas phase. Increased CO_2 fraction in the biogas also increases the hydrogenotrophic methanogenesis reaction rate, thus slightly reducing the H_2 concentration. Upon the start of the low pH perturbation, the reactor pH decreased rapidly from 7.3 to 6.4 (Figure 24). The most dramatic decrease in pH (0.4 units) occurred over the first 5.25 hours and then the pH gradually decreased to a new steady-state value of 6.5 after 23 hours.

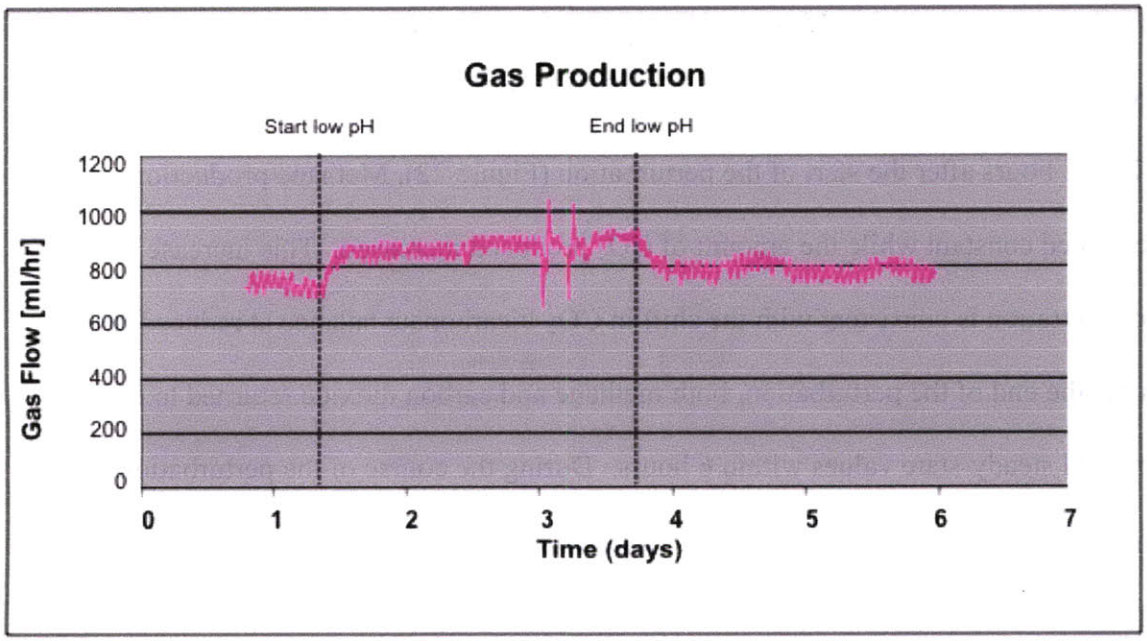

Figure 20. Gas production during low pH perturbation.

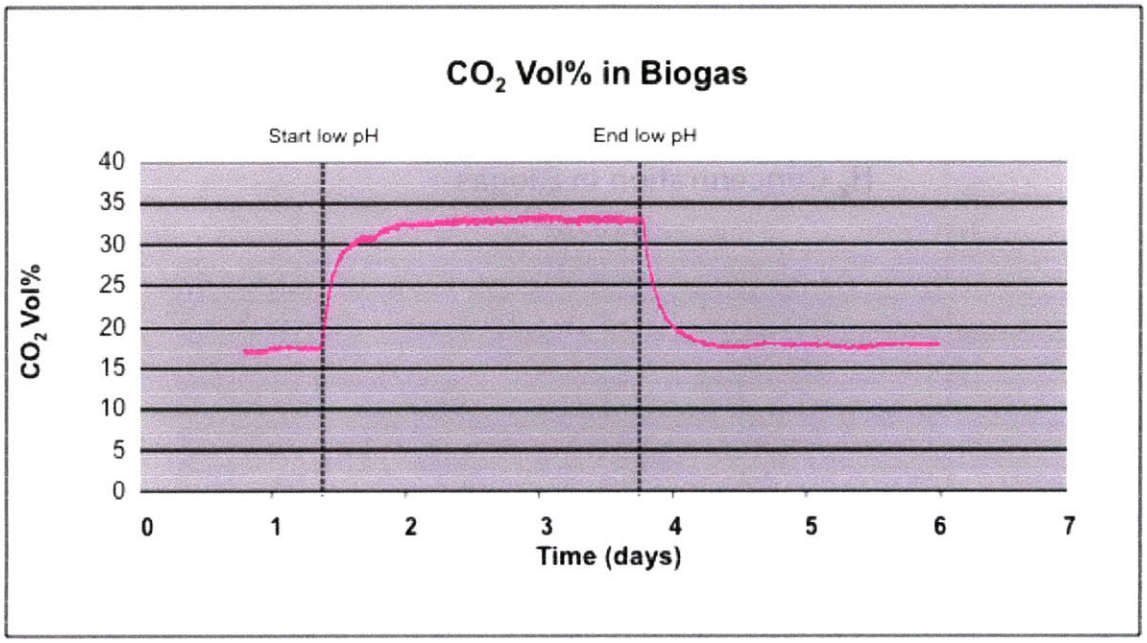

Figure 21. Carbon dioxide fraction in biogas during low pH perturbation.

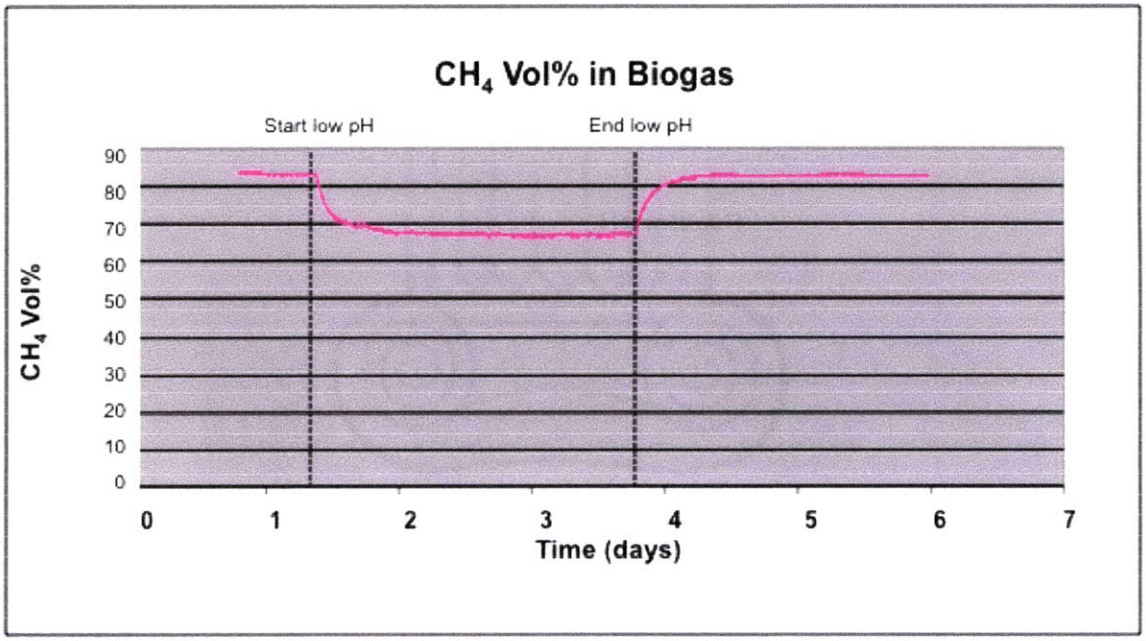

Figure 22. Methane fraction in biogas during low pH perturbation.

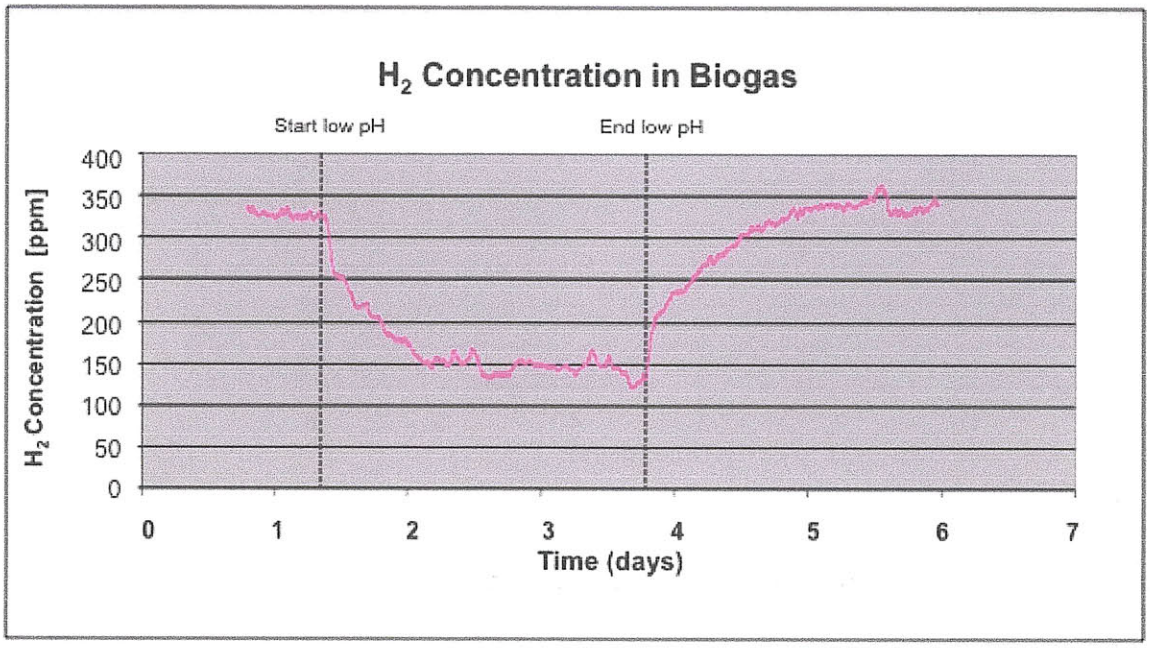

Figure 23. Hydrogen concentration in biogas during low pH perturbation.

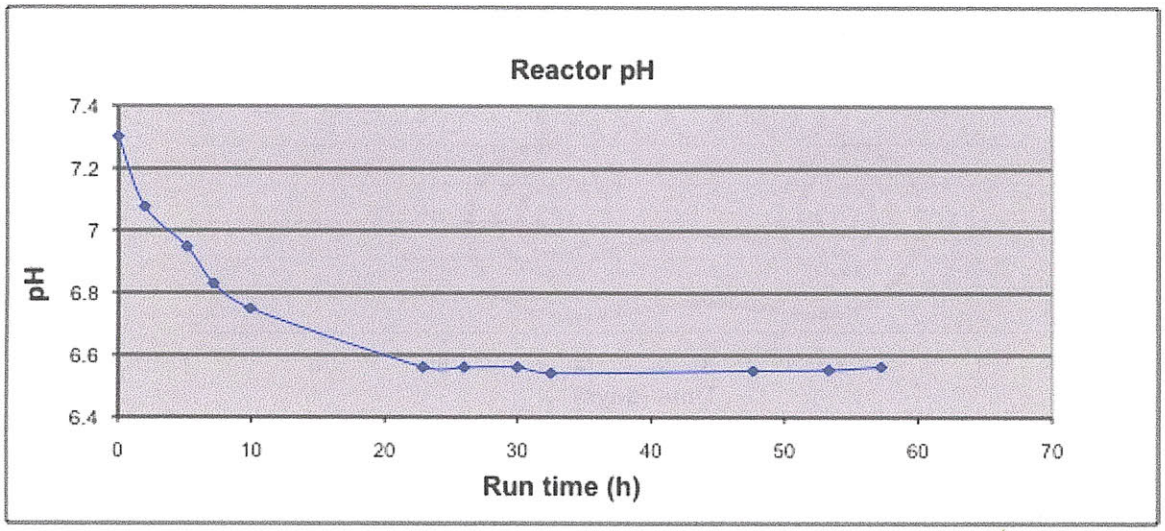

Figure 24. Reactor pH during low pH perturbation.

Discussion

Reactor Performance Under Variations

In looking at reactor operation over the course of the study, it is clear that the granules were sufficiently active to handle variations in sulfate concentration, feed concentration, organic loading rate, and pH without a significant reduction in reactor operating efficiency. Even in cases where the feed was interrupted and gas production decreased, the reactor recovered its performance as soon as the feed was restored. This type of performance is encouraging and shows that perhaps the microbial community is more stable than previously thought. When OLR was doubled and tripled, reactor pH remained constant, gas production remained constant, and the methane fraction in the biogas remained constant. No significant washout of biomass occurred and the granules maintained their structure. This shows that even despite these increases in organic loading, the microorganisms within the granules remained in balance. Future experimental plans include a 4x OLR increase to push the reactors to the operational limit.

The reactor was also able to withstand a low pH perturbation for 2.5 days. While the pH of the reactor approached the lower limit for methanogens, reactor performance did not appear to be inhibited. This can be attributed to the structure of the granules which likely maintained a higher pH inside the granule core. The reactor also sufficient buffer capacity to re-establish steady-state.

Evaluation of Monitoring Parameters

Initial results indicate that gas production and composition could be useful and inexpensive online monitoring parameters. In the event of an organic load increase, gas production was the only parameter to demonstrate a significant observable change and the increase in gas production mirrored the increase in OLR.

The results of the low pH perturbation gave insight into the utility of online gas monitoring for monitoring reactor performance and change in operating conditions. While the reactor remained stable during low pH perturbation without any apparent signs of serious upset, the online traces during the course of the perturbation were indicative of the change in reactor conditions. Within the first 2 hours of the perturbation, a significant change in the gas composition was observed (Figure 25), while pH changed only 0.2 units. This illustrates the utility of gas composition as a monitoring parameter that could be a fast and useful indicator of reactor conditions. More data will be necessary to fully evaluate hydrogen as a monitoring parameter, as the hydrogen sensor tended to drift

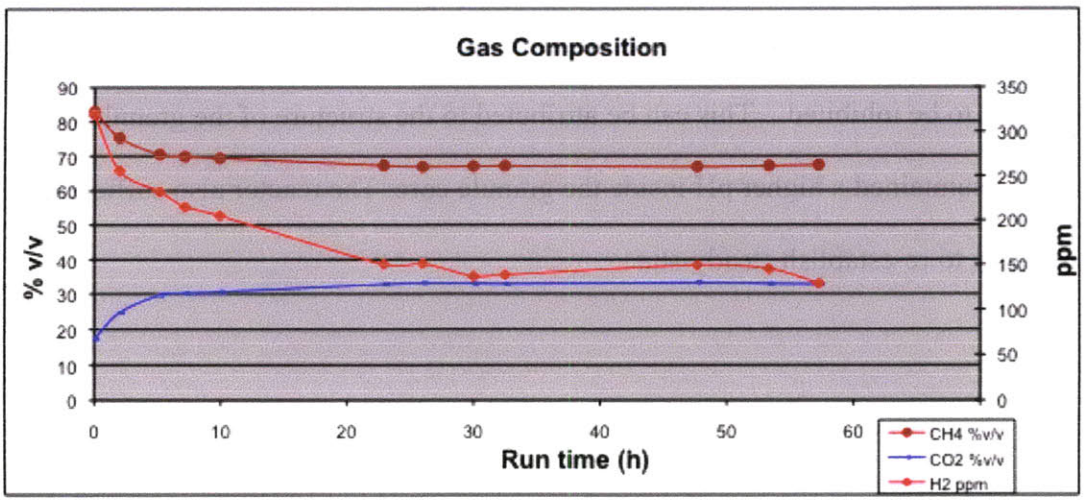

Figure 25. Evolution of gas composition during low pH perturbation.

during steady-state operation due to competition with oxygen for adsorption to the sensor surface. VFA and COD data are also useful indicators of reactor performance, and the combined online and offline data will be used to develop a simplified anaerobic digestion process model and predictive monitoring and control algorithms.

Bicarbonate alkalinity was calculated based on on-line measurements of pH and CO_2 after Day 75 (Eq. 1, Figure 26). During steady-state operation, the alkalinity was on average 2042 mg/L, which falls within the recommended range for stable anaerobic digestion illustrated by McCarty in Figure 6. During the low pH perturbation, the bicarbonate alkalinity decreased to 620 mg/L. Although the alkalinity decreased to a value outside the normal limits, as soon as the pH of the feed concentrate was increased back to normal, the alkalinity increased again back to steady state. This shows that the reactor had sufficient alkalinity to deal with the pH change. The calculated values for alkalinity tended to be higher than experimental measurements due to the fact that carbon dioxide is lost from the samples once they are are removed from the reactor and reach a new equilibrium with the atmosphere.

$$pH = pK_1 + \log \frac{\frac{\text{Alkalinity(bicarb)}}{50{,}000}}{\frac{[CO_2(g)]}{K_H}} \qquad \text{(Eq. 1)}$$

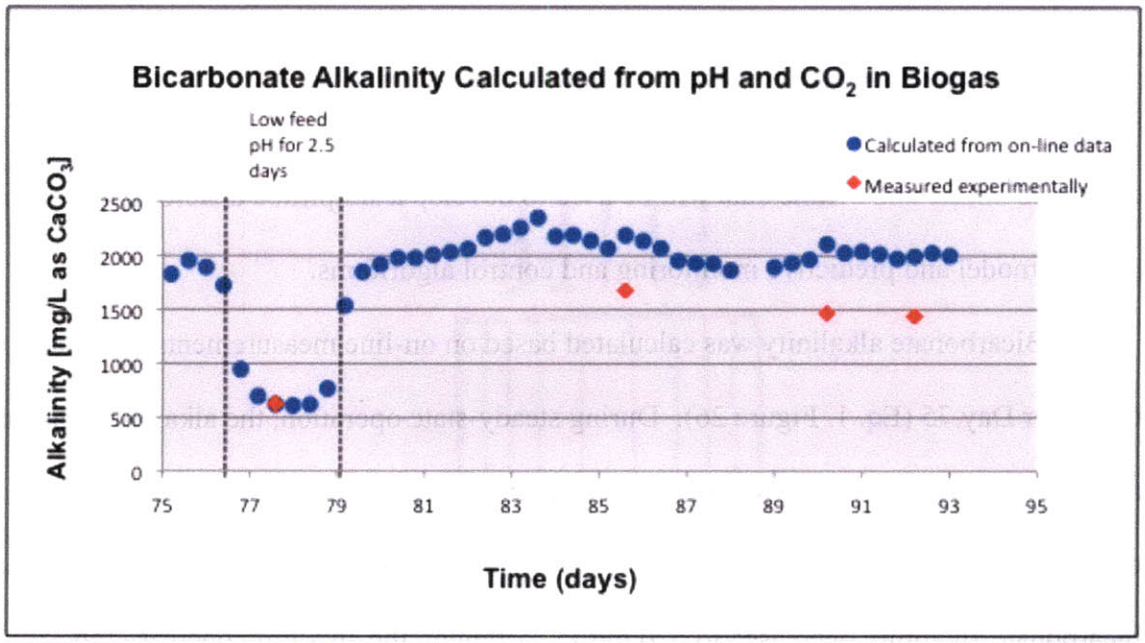

Figure 26. Bicarbonate alkalinity during low pH perturbation and steady-state operation.

While on-line monitors for alkalinity are not currently available in industry, these results show that bicarbonate alkalinity can be accurately approximated from more readily available on-line pH and gas composition sensors. Changes in alkalinity during a perturbation were clearly captured in pH and carbon dioxide measurements. This suggests that on-line measurements for pH and gas composition could be used in the model to infer parameters such as alkalinity that are difficult to measure.

Conclusions and Future Work

Overall, the experiments performed in this study showed that lab-scale anaerobic digesters were stable during variations in process conditions. The UASB reactor operated efficiently despite variations in OLR and pH, and there were no impacts to the structure of granules. Future experiments will push the lab-scale reactors to the

operational limits to determine which parameters are most important for monitoring the changes that occur. In addition, scaling issues will be considered and a pilot study will be performed to evaluate the monitoring parameters on a larger scale. Initial perturbations in organic loading rate and influent pH suggest that the gas composition and gas production appear to be the best online monitoring parameters to indicate changes in reactor conditions. However, further data is needed to fully evaluate and compare online and offline parameters to supplement the monitoring and controls algorithms. Overall, the results suggest that the reactors were relatively stable under varying conditions. These experiments and the supervisory control models which will be informed by the experimental data will encourage confidence and widespread adoption of anaerobic digestion as a wastewater treatment option.

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