

ENHANCED BIOGAS PRODUCTION THROUGH THE OPTIMIZATION OF THE ANAEROBIC  
DIGESTION OF SEWAGE SLUDGE

by

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A THESIS

Submitted in partial fulfillment of the requirements  
for the degree of Master of Science  
in the Department of Chemical and Biological Engineering  
in the Graduate School  
of The University of Alabama

TUSCALOOSA, ALABAMA

2011

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## ABSTRACT

The anaerobic digestion of sewage sludge has long been used for solids reduction by wastewater treatment facilities, but has gained recognition as a form of energy production. Biogas is formed as a byproduct of anaerobic digestion and is composed mostly of methane and carbon dioxide with other trace elements. The focus of this thesis is the enhancement of biogas production through the optimization of the anaerobic digestion of sewage sludge.

Batch experiments showed that digest pH is indicative of the current stage of digestion. This will provide wastewater treatment facilities with a way to monitor digester activity, as each stage of digestion was identified through constant pH monitoring. The digestion process was optimized through various parametric studies designed to determine the effect of each parameter and find an optimal range for operation. The optimum range for pH was 7.0-7.5. Testing of temperature showed that the mesophilic range (30-40°C) provided the highest, most constant gas production. Alkalinity adjustment with magnesium hydroxide increased both pH and alkalinity. Biogas production was highest in samples with alkalinity ranging from 2,000-2,500 mg/L as CaCO<sub>3</sub>. Volatile fatty acid (VFA) adjustment with sodium propionate increased both alkalinity and VFA content within the digest. High levels of VFA caused digestion to struggle while small adjustments showed an increase in production. Pressure measurement showed that an increase in pressure during digestion improved both the quality and quantity of produced biogas.

Semi-continuous experimentation showed consistent biogas production. However, high VFA content resulted in poor gas quality.

Digester energy balances completed at the Hilliard-Fletcher Wastewater Treatment Plant showed that  $1,705 \frac{m^3}{day}$  biogas are required for daily operation (basis: 60:40 ratio CH<sub>4</sub>:CO<sub>2</sub>). Parametric tests showed the ability to provide up to  $1,944 \frac{m^3}{day}$  at a methane content of 80%. Increasing the methane content from 60 to 80% increases the heating value of the gas by one-third, requiring less gas for daily operation. This allows for better energy efficiency. All gas volumes are reported at atmospheric pressure and a temperature of 35°C. Future work will focus on the effect of pressure to identify the extent with which it affects digestion.

## ACKNOWLEDGEMENTS

I would first like to thank my advisor, Dr. Stephen Ritchie, for his continuous support and encouragement throughout the last 2-½ years, and also for his counseling and patience throughout the research period. It was a great learning experience working with him and his editorial help in preparing this thesis is greatly appreciated. I would also like to thank the other members of my committee, Drs. Peter Clark and Perry Churchill, for their help in completing this research.

In addition, I am thankful to the collaborators with whom I have had the pleasure of working with in my time at Alabama. The help obtained from Mr. Jimmy Junkin, Mr. Keith Hardemon, Mrs. Christy Heaps, and many others at the Hilliard-Fletcher Wastewater Treatment Plant was invaluable. I also want to thank the faculty, staff and graduate students of the Department of Chemical and Biological Engineering for making this research journey an enjoyable experience, in particular Jayraj Shethji and James Bennett, for their help and support. The financial support from the Alabama Department of Economic and Community Affairs and Department of Chemical and Biological Engineering is also gratefully acknowledged and appreciated.

Finally, I want to thank my wonderful wife, Jill, and my family for their continuous encouragement and support through the past few years, as well as their continued faith in me. I could not have done any of this without my faith in Christ, who strengthens me!

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## **CHAPTER ONE INTRODUCTION**

### **1.1 Environmental Background**

In recent years, there has been an increasing desire for the use of renewable fuels, not only to reduce dependence on petroleum fuels, but also to improve upon the harm caused by fossil fuels to the environment [1-10]. Biomass is a primary feedstock for production of alternative fuels and alternative fuel precursors. Four types of conversion processes are used to break down biomass, including thermo-chemical, biological, chemical, and physical processes. When coupled with methods such as fermentation, combustion, and anaerobic digestion, the result is multiple alternative fuels such as biogas and ethanol, and precursors such as cellulose that can be further degraded to ethanol [11]. Some of these fuels can be used directly as produced and some may require cleaning to prevent corrosion during use of machinery or pipeline transport [12].

First and second generation bio-fuels, those produced from food sources and woody biomass, respectively, are seen as keys to reducing the dependence on petroleum fuels. The downfall of each is that current production does not meet the enormous supply needed for large-scale use. In 2007, the US Congress passed legislation requiring production of 34 billion liters of bio-fuels in 2008, with this number increasing to 57.5 billion liters by 2012. This equates to a little over 360 million barrels of bio-fuels by the year 2012 [13]. The

United States alone consumes over 7.5 billion barrels of oil per year, more than twenty times the amount of bio-fuels projected to be produced in 2012 [14].

The processes used for the production of bio-fuels can be very costly. Often times, the production of bio-fuels is supported through government assistance such as quotas, tax exemptions, or direct production subsidies [15]. Without this support, the cost of producing many bio-fuels is not economically competitive with fossil fuel production. Bio-fuels have other economic drawbacks when compared to petroleum fuels. Feedstocks for first and second-generation bio-fuels must be grown, and therefore land availability is a concern. Transport costs must be included, and so the distance to refineries must be considered. Refining costs must also be included in the total costs, as well as the impact upon related markets such as the food industry [13,16]. This is a short list, but one that shows there is much work to be done to reduce the cost of manufacturing bio-fuels.

One bio-fuel that has an advantage when compared to others is biogas. Its advantage is based upon the vast supply and type of feedstock for biogas production. Biogas is produced from the anaerobic digestion of organic matter, such as sewage sludge, biodegradable wastes, municipal solid waste, and manure. It is mostly composed of methane and carbon dioxide, with methane making up on average 60.5–65.5% (mole) of the gas [17]. The advantage of biogas production is that it is formed as a side product of anaerobic digestion. There are no new land requirements for growing feed. Chemical costs may be needed for cleaning, but biogas can also be used directly as formed in some cases, requiring no extra costs [12]. As long as wastewater treatment facilities continue to utilize anaerobic digestion, biogas will always be produced.

While first and second generation biofuels have been aimed at the replacement of fossil fuels in the transportation sector, biogas has the possibility of being used for heat, electricity, and transportation [18]. Although biogas is not the complete answer to reduce the dependence on fossil fuels, it does represent a cleaner fuel that can be utilized in many ways and one that will cause less harm to the environment through mitigation of green house gas (GHG) emissions [19,20]. This reduction in GHG emissions is achieved as biogas use minimizes the use of fossil fuels and carbon dioxide production [11]. This refers only to the use of biogas as the end product. For a complete environmental impact, fuel emissions from the production of biogas must be taken into account [21].

## **1.2 Anaerobic Digestion**

Anaerobic digestion is a process in which biodegradable material is broken down by microorganisms in the absence of oxygen with the end goal of managing waste and/or releasing energy. Typically during the digestion process, 30–60% of the input solids are converted into biogas, and the rest of the sludge is then dewatered and disposed of by landfill dumping [22]. By optimizing the digestion process, the amount of input solids digested can increase, allowing for less landfill dumping and an increase in the amount of produced biogas. Research on the digestion process has identified four distinct steps leading to the production of biogas, and each of these steps has a unique set of bacteria [22-24]. The difficulty presented here is that each set of bacteria has optimal conditions, and not all of these overlap [12,17]. Finding an optimal set of conditions in which each set of bacteria can thrive should show an increase in gas production.

### **1.3 Project Description**

The hypothesis of this research is that optimization of the parameters of the anaerobic digestion of sewage sludge will lead to an increase in the production of biogas. The working parameters of an anaerobic digester are defined here as temperature, pH, alkalinity, and volatile fatty acid content. Completion of lab scale parametric studies will determine what affect each has upon biogas production, with the ultimate goal of enhancing the production rate on a larger system.

### **1.4 Research Objectives**

The increased production of biogas, and its subsequent use, will allow for better energy efficiency by allowing the wastewater treatment facility to lessen the need for outside resources of power and energy. This goal will be met through the following objectives:

- Complete energy balance on the anaerobic digesters at the wastewater treatment facility.
- Perform batch digestion with continuous pH measurement.
- Conduct parametric studies on pH, temperature, alkalinity, and volatile acid content.
- Operate semi-continuous system at conditions identified in parametric study.

## **CHAPTER TWO BACKGROUND & THEORY**

### **2.1 Introduction**

The focus of this work is the increased production of biogas from the anaerobic digestion of sewage sludge. To acquire an adequate understanding of this process, it is essential to examine the details of anaerobic digestion, the make-up of sewage sludge, the parameters affecting the digestion process, and the uses and benefits of biogas. This will be done through a review of theory and previous research in these areas.

### **2.2 Anaerobic Digestion**

Anaerobic digestion is one of the oldest and most widely used methods for the reduction of solids and the destruction of pathogens. It has been used primarily at larger wastewater treatment facilities (>5 million gallons per day), but one of its many advantages is its availability at all scales, large or small [22]. Process advantages and disadvantages are often made in comparison to other secondary treatments, primarily aerobic treatment. Table 2.1 gives an overview of the advantages and disadvantages of anaerobic digestion. The process advantages far outweigh the disadvantages, but the initial capital costs can deter treatment facilities from its use. Therefore, optimizing the use of anaerobic digestion is a necessity to offset the costs associated with start-up.

**Table 2.1 Advantages and disadvantages of anaerobic digestion [22,25]**

<b>Advantages</b>	<b>Disadvantages</b>
Production of biogas	High capital costs
Reduction of total sludge mass	Highly sensitive microorganisms
Low odor content of digested solids	Long retention times
High rate of pathogen inactivation	
High nutrient composition of digestate (used as fertilizer)	
Small and large scale applications	

### **2.2.1 History**

Anaerobic digestion has long been used for wastewater treatment, mainly to reduce sludge volume and disposal costs [12]. Scientific interest in the digestion process can be dated back to 1682 when Boyle and Papin detected gas being released from decomposing organic matter [26]. It was approximately another century before Volta realized that the gas being released was methane, and yet another century passed by before Bechamp discovered that a microbiological process was the cause for gas formation from decomposing organic matter [26]. The first recognized use of anaerobic digestion commercially was seen in the middle to late 19<sup>th</sup> century in India and France. In India, anaerobic digestion was used in a small leper colony, while in France it was used to reduce the mass of suspended organic material in municipal wastewater [27,28]. Which was first between these two countries can be debated, but it is known that the development and application of the digestion process was understood long before the chemistry and microbiology. Scientific research into the process of digestion was seen in the early 1930's when scientists completed numerous studies leading to a better understanding of factors affecting digestion [29,30]. The first use of biogas to any extent was seen in Germany around the turn of the 20<sup>th</sup> century to fuel street lamps in the vicinity of a water treatment plant [31]. This utilization of biogas has ballooned into multiple uses in the ever growing field of alternative fuels [32]. The ability of biogas to be utilized for electricity production and other sources of energy has led to the current research into developing ways to improve the gas production from anaerobic digestion and allow wastewater treatment plants to lessen their dependence upon outside sources of energy.

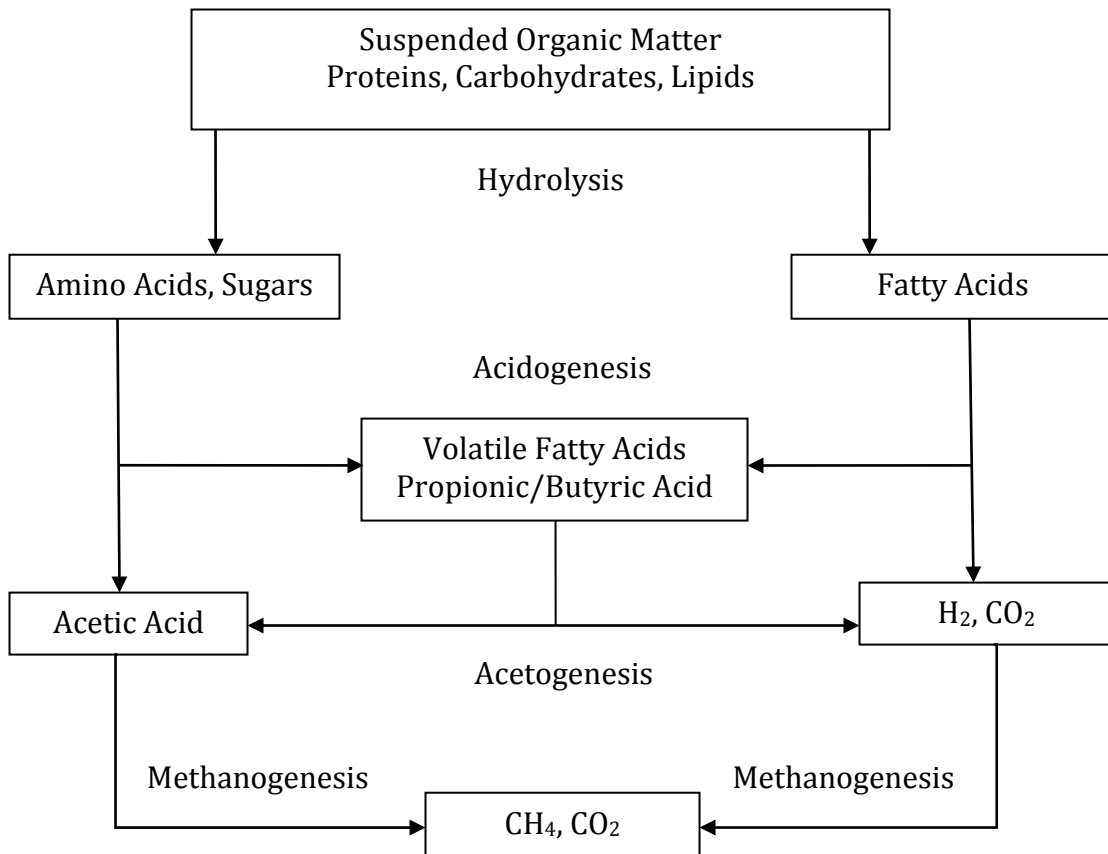
## **2.2.2 Process of Digestion**

The digestion process is composed of four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The mechanisms and conditions for digestion will be discussed for each of the four processes, along with an in-depth look at the bacterial presence behind each. The discussion will be based upon the breakdown of sewage sludge. Figure 2.1 shows a schematic breakdown of the digestion process and the products formed. Looking at Figure 2.1, it is convenient to see each of the stages of digestion independently, but all four occur simultaneously within a digester. The microorganisms involved with each phase are metabolically dependent upon each other for survival. For instance, methanogenic bacteria depend upon the end products of acetogenesis for survival, and acetogenic bacteria rely upon the methanogens to break down volatile fatty acids so that they do not become inhibited by their own end products. This relationship and others will be discussed in further detail below.

### **2.2.2.1 Hydrolysis**

The hydrolysis of sewage sludge consists of breaking down complex particulate matter into lower molecular weight compounds. Larger organic compounds such as proteins, carbohydrates, and lipids are hydrolyzed into smaller units such as amino acids, sugars, and long-chain fatty acids (Figure 2.1). Hydrolysis has been seen to be the rate-limiting step of the digestion process at temperatures below 20°C [33-35].

Hydrolytic enzymes, such as proteases, cellulases, and lipases, control the extracellular enzymatic reactions taking place during hydrolysis. The role of these enzymes is to break down complex molecules into units that can be taken in by the microbial cell.



**Figure 2.1 Schematic breakdown of anaerobic digestion process [33]**

The production of protease is much more than needed, estimated at fifty times the amount required for hydrolysis. Proteolytic bacteria can reach concentrations of approximately  $6.5 \times 10^7 \text{ ml}^{-1}$ , while lipolytic and cellulolytic bacteria have concentrations of  $7 \times 10^4 \text{ ml}^{-1}$  and  $10^4\text{-}10^5 \text{ ml}^{-1}$ , respectively [23]. All hydrolytic bacteria are very stable throughout a wide pH range (5.0–11.0) [36].

One type of inhibition observed during hydrolysis is product inhibition. The synthesis of extracellular enzymes by the hydrolyzing bacteria is partly governed by the substrate and product concentrations in the digester liquor [36]. End-product inhibition of extracellular proteases by amino acids has been observed, and they may also be repressed by glucose. This suggests that high concentrations of hydrolysis products will inhibit the formation of extracellular enzymes from hydrolytic bacteria [37]. Consequently, an accumulation of hydrolysis end products can slow down hydrolysis, which may eventually lead to a breakdown of the digestion process.

#### **2.2.2.2 Acidogenesis**

Acidogenesis, also known as the beginning of fermentation, continues the breakdown of the smaller sub-units from hydrolysis, and forms multiple organic acids along with hydrogen and carbon dioxide (Figure 2.1). This step in the digestion process is often the fastest and it provides a high-energy yield for the microorganisms [38]. The products of hydrolysis are broken down by fermentative bacteria to form simple organic compounds, most prominently volatile fatty acids, such as butyric and propionic acids, along with hydrogen, carbon dioxide, and acetic acid [33,39]. The process of acidogenesis is completed by both facultative and obligate anaerobes, with the dominant of the two

differing among researchers [33,25]. Having a large number of facultative anaerobes is important as they can metabolize through the oxidative pathway, allowing them to remove any dissolved oxygen present in the mixture. The ability of facultative anaerobes to remove oxygen is key to maintaining a smooth digestion process as methanogens are obligate anaerobes. Obligate anaerobes cannot operate through the oxidative pathway as oxygen is toxic to them. If the facultative anaerobes do not remove dissolved oxygen within the system, digestion can become inhibited [25].

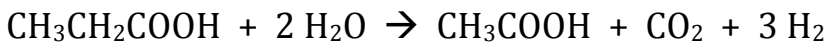
### **2.2.2.3 Acetogenesis**

During acetogenesis, volatile fatty acids are broken down to form acetate, hydrogen, and carbon dioxide (Figure 2.1). These end products are also formed during the acidogenesis phase, but complete acid breakdown is achieved during acetogenesis in preparation for the formation of biogas through methanogenesis. Figure 2.2 shows the breakdown of propionic and butyric acids to form methane. The first step represents the actions of acetogenic bacteria, while the second step is seen during methanogenesis. The main product of acetogenesis, acetate, is the most important compound produced during the fermentation stage of the digestion process, with fermentation comprising both acidogenesis and acetogenesis [40]. This is because approximately 70% of methanogens utilize the acetoclastic pathway to form methane [23].

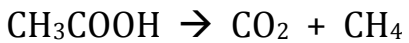
Since acetogenesis and methanogenesis occur simultaneously during the digestion process, the products of acetogenesis are converted to biogas at the same rate at which they are formed. This is the reason for low levels of acetic acid and hydrogen in a properly

**Breakdown of propionic acid:**

***Step 1-acetogenesis***

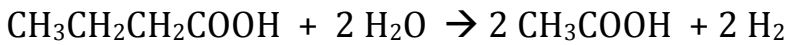


***Step 2-methanogenesis***

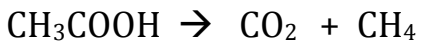


**Breakdown of butyric acid:**

***Step 1-acetogenesis***



***Step 2-methanogenesis***



**Figure 2.2 Breakdown of propionic and butyric acids to form methane [41]**

working digester, as they have no time for accumulation. Given that acid forming bacteria have doubling times measured in hours while methane formers double at rates measured in days, this balance between acetogenesis and methanogenesis is critical to maintain proper digestion [23]. Along with a much higher growth rate, acetogenic bacteria are tolerant to changes in pH and temperature [25]. This allows for optimization of the anaerobic environment to be centered on the needs of the methanogenic bacteria, as they have a narrow range of conditions suitable for biogas formation.

#### **2.2.2.4 Methanogenesis**

During the final stage of digestion, methanogenic microorganisms break down the end products of acetogenesis to form biogas, predominantly made up of methane and carbon dioxide [42]. Methanogenic microorganisms are the most sensitive to oxygen among known bacteria, and are therefore the most strictly anaerobic [36]. There are multiple types of methanogenic bacteria, comprising over fifty species classified into three orders and four families in the domain Archaeobacteria. These bacteria are classified according to their structure, substrate utilization, types of enzymes produced, and the temperature range associated with growth [17].

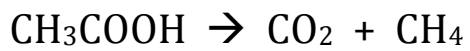
Methanogens are very sensitive to environmental changes. Even the slightest change in pH, temperature, or a number of other parameters can significantly affect the methanogenic activity. One way methanogens can overcome changes in pH is an internal buffering system. This buffering capability can be used to overcome an accumulation of volatile fatty acids formed during acidogenesis [23]. The buffering system is based upon bicarbonate in the liquid phase and carbon dioxide in the gas phase, both produced during

methanogenesis, counteracting the effect caused by acids formed during previous phases of digestion [12].

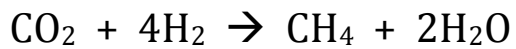
The batch kinetics of methanogenesis can be assembled into four general steps. A rapid increase of the methanogenic rate upon addition of acetate is seen first. Following this, a rate increase with time is observed due to the growth of methanogenic microorganisms. Next, a constant rate of biogas production is achieved, and finally, a rapid decline in activity occurs which is associated with acetate depletion [43]. The kinetics of methanogenesis, in large part, depend upon the growth rate expressed by methanogenic bacteria. The range of generation times for methane-forming bacteria ranges from a few days to several weeks under optimal conditions, showing the need for extended retention times [17].

The chemical breakdown of the end products of acetogenesis can be found in Figure 2.3. Acetoclastic cleavage of acetate and reduction of carbon dioxide are the two major pathways through which methane is produced. Methane formation from acetic acid and carbon dioxide each occur in a single-step process with approximately 70% of methanogens utilizing the acetoclastic pathway to form methane [23]. Acetotrophic methanogens break down acetate into methane and carbon dioxide, but are adversely affected by the accumulation of hydrogen. Hydrogenotrophic methanogens utilize hydrogen to convert carbon dioxide to methane. Since acetotrophic methanogens reproduce more slowly than hydrogenotrophic methanogens, the action of hydrogenotrophic methanogens is key to maintaining a low hydrogen partial pressure. This

### **Splitting of Acetic Acid**



### **Reduction of Carbon Dioxide**



**Figure 2.3 Multiple pathways for the formation of methane [41]**

will make certain that acetate production continues through acetogenesis and methane production continues through the acetoclastic pathway [41].

## **2.3 Sewage Sludge**

### **2.3.1 Primary Sludge**

Figure 2.4 shows the wastewater treatment process, giving schematic representation of the formation of primary sludge. Primary treatment begins once a wastewater stream has undergone preliminary treatment to remove larger materials through bar screens, and sand and gravel in grit chambers. When the wastewater enters the primary clarifying tank, settleable solids collect at the base of the tank where they are removed as primary sludge. Settleable solids range from 0.05-10 mm in size [44]. Generally speaking, primary sludge is composed of oils, greases, and larger organic material. Primary sludge can contain up to 70% of the suspended solids in a wastewater stream and up to 40% of the biochemical oxygen demand (BOD) [23]. The total solids concentration varies between 2–7% [25].

### **2.3.2 Waste-Activated Sludge**

Waste-activated sludge (WAS) has undergone secondary treatment during the wastewater treatment process before being sent to digestion tanks. Secondary treatment begins at the completion of primary treatment, in which the wastewater is pumped from the primary clarifying tanks into the aerobic digesting tanks. During the activated sludge process, microorganisms are introduced to wastewater to continue the breakdown of suspended organic solids and biodegradable material, reducing the oxygen demand of the

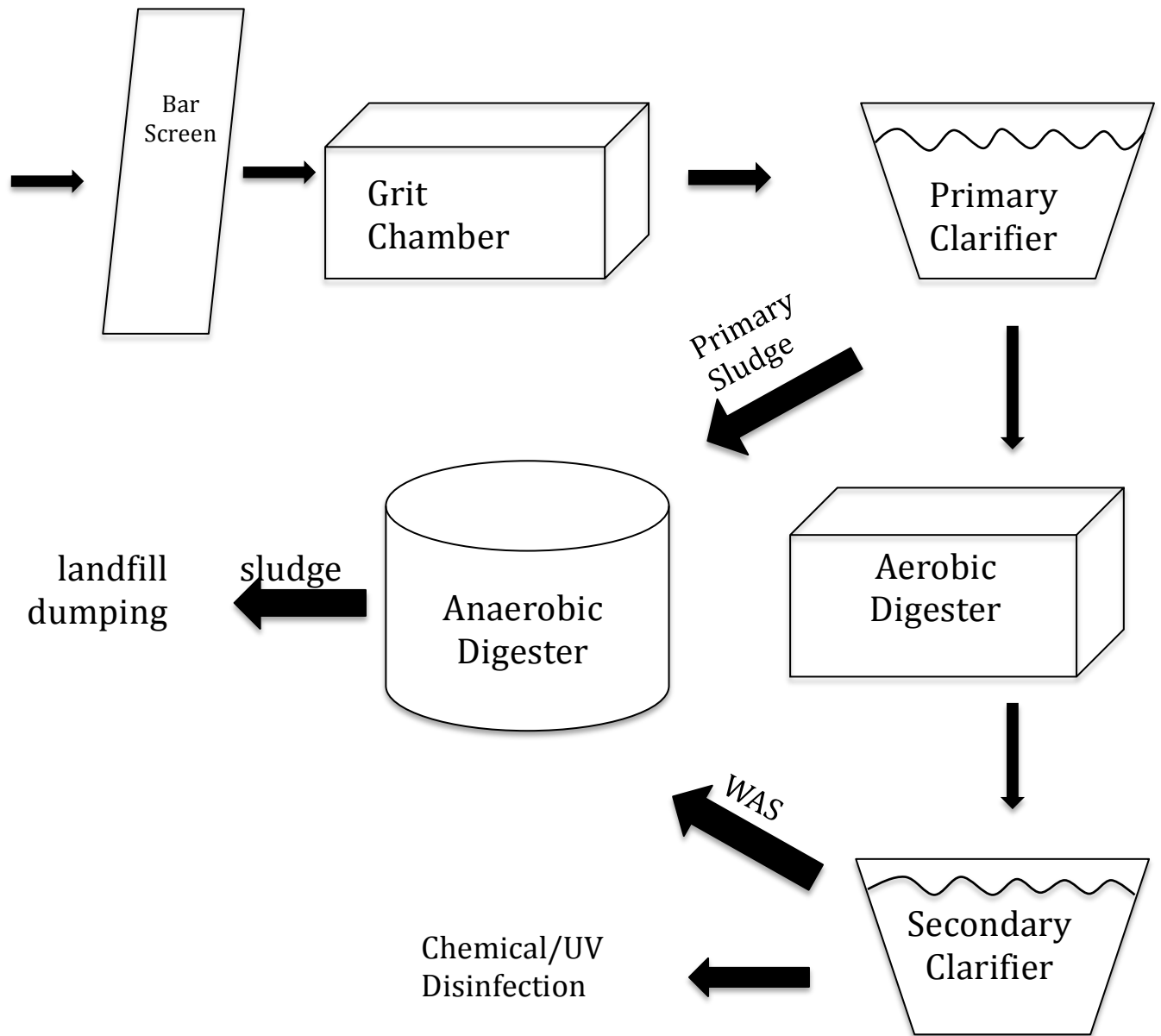
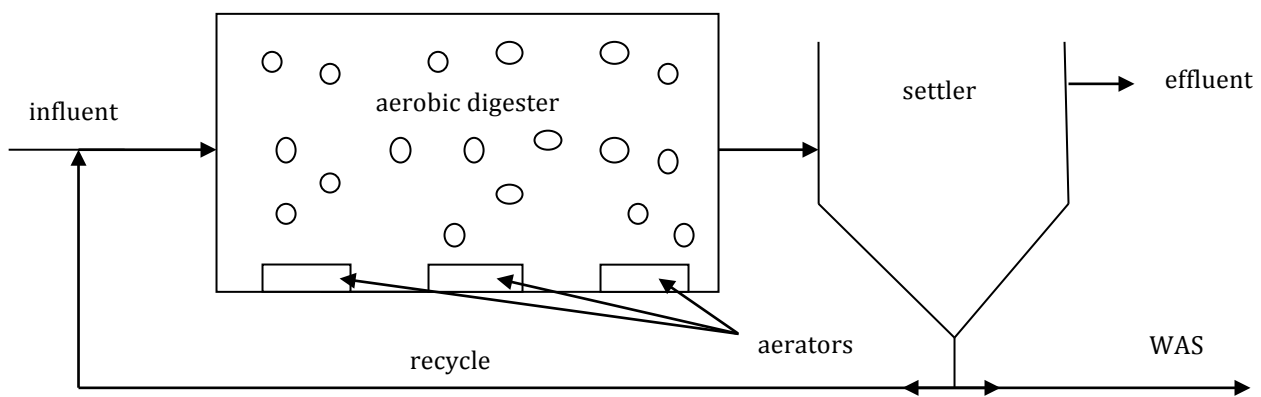


Figure 2.4 Wastewater treatment process (unless noted, arrows indicate flow of water)

influent stream. These microorganisms feed upon the suspended solids, forming sludge flocs that are upheld in the mixed liquor by the agitation of aeration, which provides the needed amount of oxygen for aerobic consumption. The bacteria are constantly being washed out of the aerobic reactor into the secondary clarifying tank by the incoming sewage stream. Here, liquid-solid separation occurs, and the waste-activated sludge is either sent for anaerobic digestion or recycled back into the aerobic reactor to maintain a high microbial density to achieve sufficient BOD removal [33,44]. Figure 2.5 shows a schematic of the aerobic digestion process, leading to the production of WAS.

## **2.4 Biogas**

Biogas is formed as a result of methanogenesis during anaerobic digestion. This gas is composed mostly of methane and carbon dioxide, but can also contain trace amounts of hydrogen sulfide, nitrogen, oxygen, and hydrogen. Table 2.2 shows the typical composition of biogas generated through anaerobic digestion. As can be seen from Table 2.2, biogas has at least some value as an energy replacement option based upon its methane content. When looking at the heating values associated with biogas, one must not only account for methane, but also the heat sinks present, such as carbon dioxide and water vapor. The heating value of pure methane is 34,300 kJ/m<sup>3</sup>, while the heating value of biogas containing 40 – 80% methane ranges between 13,720 – 27,440 kJ/m<sup>3</sup> [20]. The affect of water vapor upon the heating value is not as detrimental as carbon dioxide, but it can alter the flame temperature, flammability limits, and the fuel-to-air ratio for combustion. Depending on the temperature during digestion, the amount of water vapor in a sample of biogas may be as high as 6.6% (volumetric), equating to a water content of 50 mg of water vapor per liter



**Figure 2.5 Aerobic activated sludge process [33]**

**Table 2.2 General composition of biogas [20,42,45]**

<b>Gas</b>	<b>% (volume/volume)</b>
Methane	40 - 80
Carbon Dioxide	20 - 60
Hydrogen Sulfide	10 - 10,000 ppm
Nitrogen	0.05 - 1.0
Oxygen	0.022
Hydrogen	< 0.01
Water Vapor	1

of biogas [20]. Figure 2.6 shows the effect of water vapor on the heating value of biogas. By way of the graph, the heating value of biogas decreases an average of 10% with the addition of 50 mg H<sub>2</sub>O/L biogas. A decrease of this nature shows the necessity for the removal of water vapor before use in order to achieve the maximum heating value.

Biogas can be used either raw or upgraded in many applications. The most common uses of biogas are for electricity generation/co-generation, vehicle fuel, production of chemicals, injection into the natural gas grid, and as an industrial energy source for heat, steam, and cooling [32]. The biggest obstacle for increased biogas use is gas cleaning. Biogas cleaning is of interest because its contaminants negatively impact machine parts and pipeline metal. For example, hydrogen sulfide has been shown to aggressively corrode metal structures at concentrations as low as 50 ppm [46]. Carbon dioxide does not have the same effect as hydrogen sulfide, but it does reduce the heating value of the gas. Methods being used to remove carbon dioxide and hydrogen sulfide include absorption and adsorption, while cryogenic separation and membrane separation are gaining interest [47-49]. Adsorption onto various solids at high temperatures and high pressures gives 80% methane that can be directly inserted into the natural gas network, but it is costly due to operational conditions [45,50]. Cryogenic separation is very effective, providing 97% pure methane, but has not been adequately tested. It is expected to be used to produce vehicle quality methane. This method is also very expensive due to high operational costs and has only been tested at pilot-scale [50]. Biological cleaning has also been successful at lowering the hydrogen sulfide content below 100 ppm [32]. Organic solvents, such as polyethyleneglycol or alkanol amines, can remove both carbon dioxide and hydrogen sulfide. Both contaminants are more soluble than methane, and will dissolve at

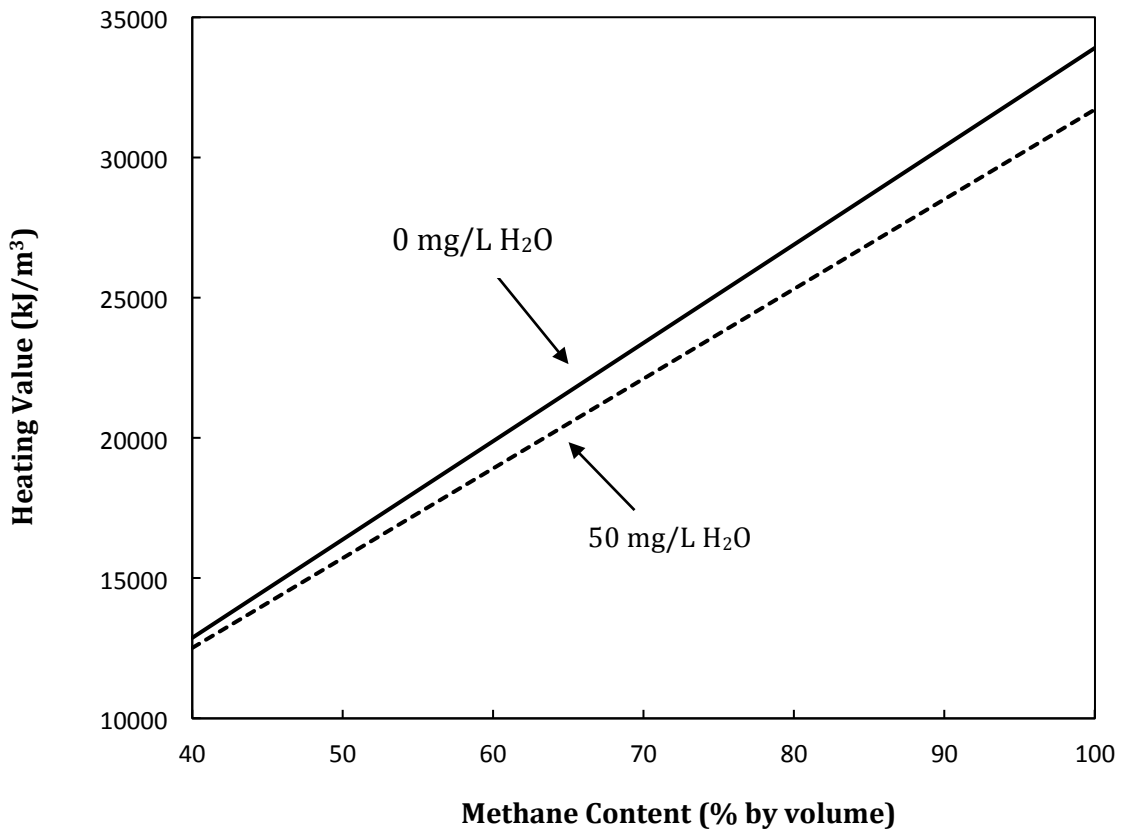


Figure 2.6 Affect of water vapor on heating value of biogas (adapted from [20])

low-pressure operation. Upon saturation, the solvents are regenerated using steam. These solvents show promise, reducing carbon dioxide to 0.5 – 1.0 vol% in biogas [12].

## **2.5 Parameters of Interest**

Optimized operation of the anaerobic digester is a function of numerous, coupled, dependent variables. Consequently, a rapid change in one parameter of an anaerobic digestion system can initiate a chain reaction of effects that may eventually lead to inhibition of the digestion process. For instance, when methanogenic bacteria are not operating properly, acid build-up is seen in the digester. This causes the acetogenesis and acidogenesis phases to operate poorly because of a high hydrogen partial pressure. Hydrolysis would also be affected, as end-product inhibition would occur if the acidogenesis phase was not functioning [23,25,37]. When these parameters are controlled under optimal conditions, the digestion process is efficient and stable. The range of operation of each parameter and their individual affect upon digestion will be discussed below.

### **2.5.1 pH**

Monitoring and maintaining the pH throughout digestion is vital to the success of the anaerobic process. Different microorganisms within the digest have different optimum pH values, but the most important of these are the methanogens. The first three phases of digestion (Figure 2.1) have microorganisms that are capable of working over a large pH range, while methanogens operate within a much narrower pH range, typically between pH 6.5–7.5. A pH range of 4.0–8.5 is acceptable for the continuation of activity for hydrolysis, acidogenesis, and acetogenesis [12,25,33]. Deviation from the optimized pH range of

methanogens results in a greater decrease in methanogenic activity, which leads to a build-up of acetogenesis end products. This causes the pH to drop further due to the increased amount of VFAs in the system. If this action is left uncorrected, continued accumulation of acids will result in a cessation of methanogenic activity, causing the digester to “sour” [51]. Therefore, it is of high priority to maintain an optimized pH for methanogenic activity to ensure the continued operation of the digestion process.

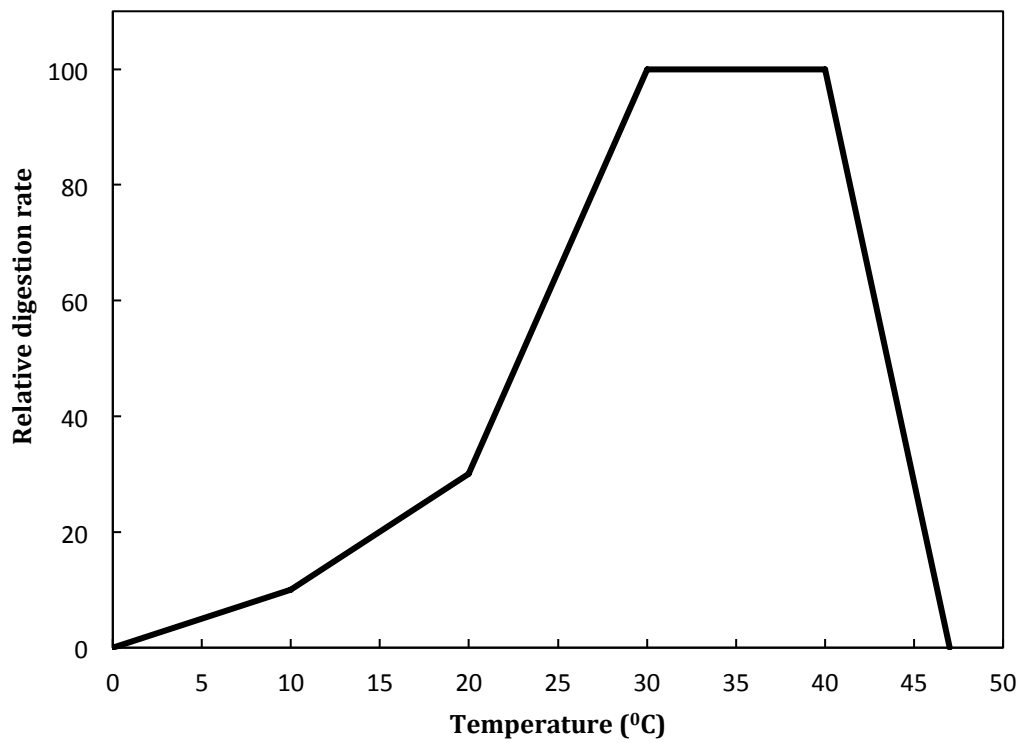
### **2.5.2 Temperature**

Temperature can influence the rate of bacterial action as well as the quantity of moisture in the biogas, as moisture content increases exponentially with temperature. Temperature also has an influence upon the concentration of contaminants in biogas [22]. Temperature fluctuations can be very harmful to the digestion process, specifically to the methanogenic bacteria. Typically, mesophilic bacteria can withstand temperature fluctuations of  $\pm 3^{\circ}\text{C}$  without noticeable reduction in the production of biogas, but it is important to keep the temperature constant throughout the digestion process [24].

Determining what range of temperature will be used is of paramount importance as mesophilic and thermophilic ranges offer many advantages and disadvantages as seen in Table 2.3. There are benefits to both temperature ranges, but the stability offered by mesophilic bacteria is a large reason for its worldwide use. As seen in Figure 2.7, operation within the mesophilic range is stable, but straying outside this range results in the rate of digestion plummeting to zero. Methanogenic diversity is often low among treatment plants operating at thermophilic temperatures, making these operations even more sensitive to changes in temperature. The difference in energy requirements also plays a large role, as

**Table 2.3 Comparison and contrast of mesophilic and thermophilic temperature ranges [22]**

<b>Mesophilic (30 - 40°C)</b>	<b>Thermophilic (50 - 60°C)</b>
Less energy for temperature maintenance	Increased solids reduction
Less odor potential	Higher metabolic rate
Lower bacterial death rate	Increased destruction of pathogens
Lower effluent VFA concentrations	Higher specific growth rate of methanogens
Higher stability	Reduced retention times



**Figure 2.7 Digestion rate as a function of temperature looking at the mesophilic range [33]**

the amount of energy required to maintain a thermophilic environment cannot always be met by the produced biogas alone [25]. If this is the case, then a major benefit to anaerobic digestion has been lost.

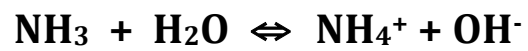
### **2.5.3 Alkalinity**

The alkalinity of an aqueous solution is its acid-neutralizing capacity [52]. Sufficient alkalinity must be present for the proper control of pH. The components most affecting the alkalinity of a digester are the equilibrium between carbon dioxide and bicarbonate and that between ammonia and ammonium, with the most dominant determined by the feed sludge. For instance, a feed sludge high in proteinaceous wastes is associated with high alkalinity due to the release of amino groups and ammonia production [23]. Alkalinity is mostly present in the form of carbon dioxide in the gas phase and bicarbonate in the liquid phase. Carbon dioxide is released through the degradation of organic compounds and both CO<sub>2</sub> and ammonia are released through the breakdown of amino acids and proteins [17]. Looking at Figure 2.8, the release of ammonia results in the production of ammonium, providing a major source of hydroxide needed to react with carbon dioxide to form bicarbonate [23]. Bicarbonate alkalinity within the digestion system is directly proportionate to the amount of ammonia released. The release of carbon dioxide results in the production of carbonic acid, bicarbonate, and carbonate [51]. The alkalinity in the digester is reported as calcium carbonate, as seen in Figure 2.9. Based upon the figure, normal limits of alkalinity range between 1,000 to 5,000 mg/L as CaCO<sub>3</sub> in the liquid phase and 25-45% CO<sub>2</sub> (biogas volume) in the gas phase. This helps maintain the proper pH as

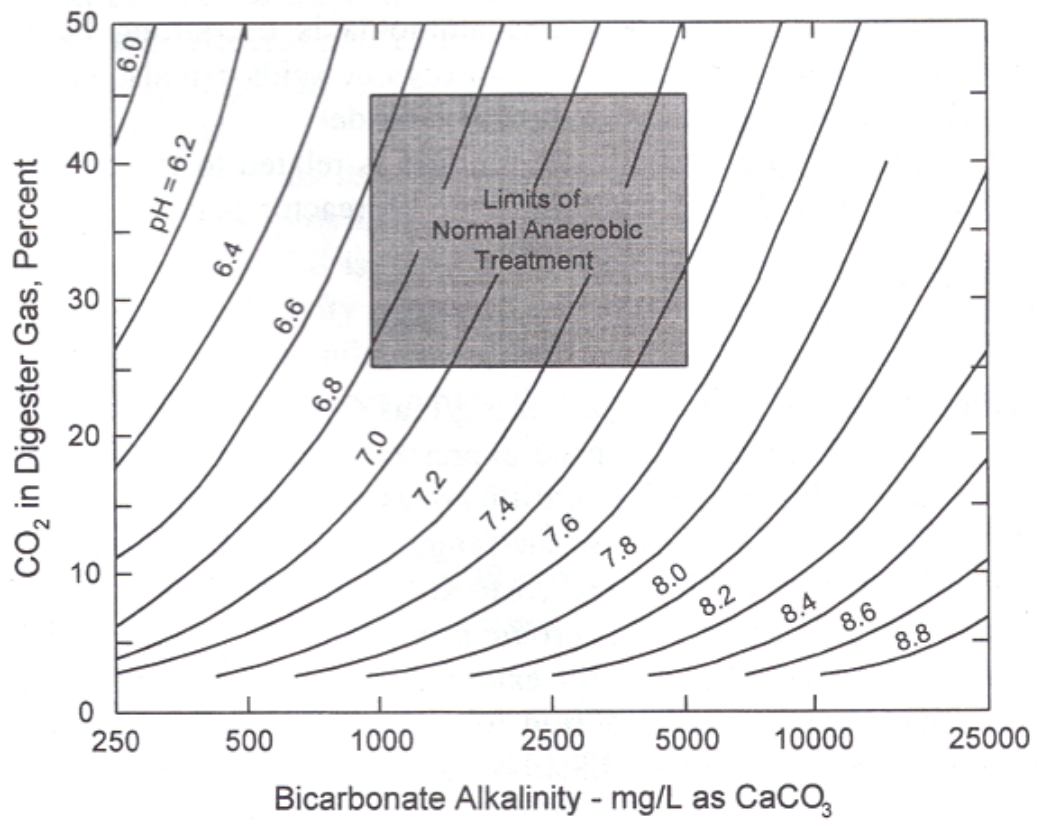
**A) Carbon Dioxide:**



**B) Ammonia:**



**Figure 2.8 Buffering reactions by A) carbon dioxide and B) ammonia [23]**



**Figure 2.9 Limits of normal anaerobic treatment for optimized pH and alkalinity [51]**

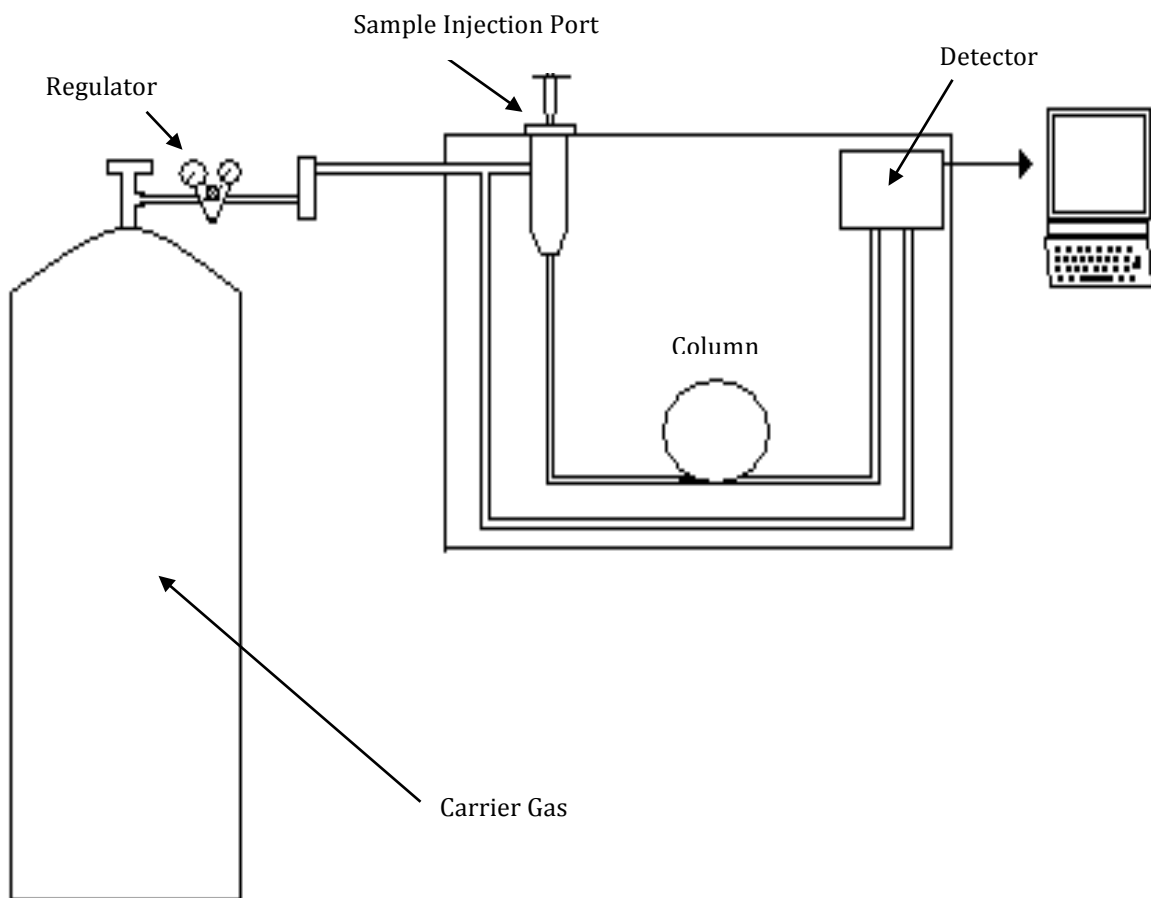
well as buffering the effect caused by VFAs. Operating within this range should ensure proper digestion along with production of a quality biogas [51].

#### **2.5.4 Volatile Fatty Acids**

Volatile fatty acids are first produced through acidogenesis during the digestion process and continue to be produced through acetogenesis. VFA content within a digester should always be minute, as acetogenesis and methanogenesis occur simultaneously, meaning that the end products of acetogenesis are degraded to methane as they are formed [23,25]. If VFAs begin to accumulate within the digester, methanogenic bacteria will become inhibited. The pH of the system would begin to drop, falling lower than 7.0, below the optimum pH for methanogenic activity. Accumulation of VFAs will also cause an increase in the hydrogen partial pressure, negatively affecting the acetotrophic methanogens, as discussed in section 2.2.2.4 [41]. Therefore, maintaining a low amount of VFAs in the reactor is essential for continued digestion. Optimum values have the amount of VFAs as low as 200 mg/L acetic acid (HAc) [42].

#### **2.6 Gas Chromatography**

Gas chromatography (GC) is a useful and accurate analysis tool that has been used for the analysis of liquid and gas mixtures since 1952. Drs. James and Martin were credited with the discovery of the analytical method while separating volatile fatty acids. After its discovery, it immediately gained recognition within the petrochemical industry [53].



**Figure 2.10 General schematic of a gas chromatograph [54]**

A gas chromatograph is made up of many working parts, but its use is rather simple. Figure 2.10 shows a generalized schematic of a gas chromatograph. To begin, a sample is input through an injection port and is subsequently separated in a column between a mobile gaseous phase and a stationary phase. Separation in the column occurs due to the affinity of the sample for the stationary phase. The mobile gaseous phase must be an inert gas, but the stationary phase can be made of either a liquid or a solid. Solid stationary phases are usually found in packed columns, made of a finely divided packing material like silica. Typically in gas-solid chromatography, separation occurs due to physical adsorption of the analytes to the solid stationary phase. Gas-solid chromatography is common for the separation of low molecular weight gaseous species. Liquid stationary phases can be found in capillary columns, often having low volatility, high thermal stability, and chemical inertness [54]. The use of a packed or capillary column depends upon the amount of resolution needed. Capillary columns provide better separation, and therefore better resolution, due to their increased length over packed columns. This increased length allows for a much larger number of theoretical plates to be present. Once separation has been completed, the sample is analyzed as the mobile phase carries each analyte to the detector.

The thermal conductivity detector (TCD) is one of the earliest and widely used methods of detection for use with a GC. The advantages of using a TCD include its simplicity, its general response to both organic and inorganic species, and its nondestructive character, permitting collection of solutes after detection if desired. The chief disadvantage to using a TCD is its relatively low sensitivity, with a detection limit of 50 pg/s, less than 0.1 ppm based upon a flow rate of 250 scc/min helium [53,54] Other detectors, such as the flame ionization detector (FID), have sensitivities exceeding that of

the TCD by factors of  $10^4$  to  $10^7$ . This low sensitivity often limits the use of a TCD to a GC containing a packed column. The detector works through identifying differences in the thermal conductivities of the gas stream exiting the column. Helium and hydrogen, two of the most prominent carrier gases, have thermal conductivities that are approximately six to ten times greater than all organic compounds. Therefore, when any organic species passes through the detector, the thermal conductivity greatly decreases, resulting in a large increase in the temperature of the TCD [54].

## **CHAPTER THREE EXPERIMENTAL PROCEDURE**

### **3.1 Introduction**

The experimental methods and techniques used in this research will be discussed in three sections, including batch testing, parametric analysis, and semi-continuous systems. Typical runs will be described for all three sections with schematic representations for each. A final review will be given to the analytical technique of gas chromatography. Multiple tests have been run upon samples of primary digested sludge, WAS, and raw primary sludge obtained from the Hilliard-Fletcher Wastewater Treatment Plant (HFWWTP) in Tuscaloosa, AL.

### **3.2 Materials**

For each experiment, fresh samples of raw primary sludge, partially digested primary sludge, and WAS were obtained from the HFWWTP at the beginning of each experiment. When not in use, samples were refrigerated at 6°C, but no samples were held longer than 1 month. In most cases, samples older than 2 weeks were not used.

Batch experiments consisted of testing upon raw and partially digested primary sludge. No pretreatment or chemical adjustment was done to the sludge before or during testing. Semi-continuous experiments tested mixtures of WAS and raw primary sludge. The only chemical addition was 10.0 M sodium propionate, made by dissolving sodium

propionate (99% pure) in deionized water. Sodium propionate was obtained from VWR International (West Chester, Pennsylvania).

Parametric studies were conducted on WAS and raw primary sludge. Parameter experiments were completed in small sample vials (40 mL). Each vial had an open top polypropylene cap containing a polytetrafluoroethylene (PTFE) lined clear silicone septum. The number of vials used in each experiment varied depending upon the range of each parameter tested, typically ranging between 24 – 36 vials. A water bath was used as the heat source for each experiment. Parametric adjustment of pH was performed using 1.0 N sodium bicarbonate (99.7 – 100.3%) and 1.0 N hydrochloric acid (36.5 – 38%). Parametric adjustment of alkalinity was completed using 15.0 N magnesium hydroxide (95%) and 0.1 N sulfuric acid (95 – 98%). Volatile fatty acid content was altered using 1.0 and 10.0 M sodium propionate (99%, VWR). Chemicals were used in solution and were prepared with deionized water. All chemicals were purchased from either VWR International (West Chester, Pennsylvania) or Fisher Scientific (Pittsburgh, Pennsylvania). The tested range of each parameter can be found in Table 3.1

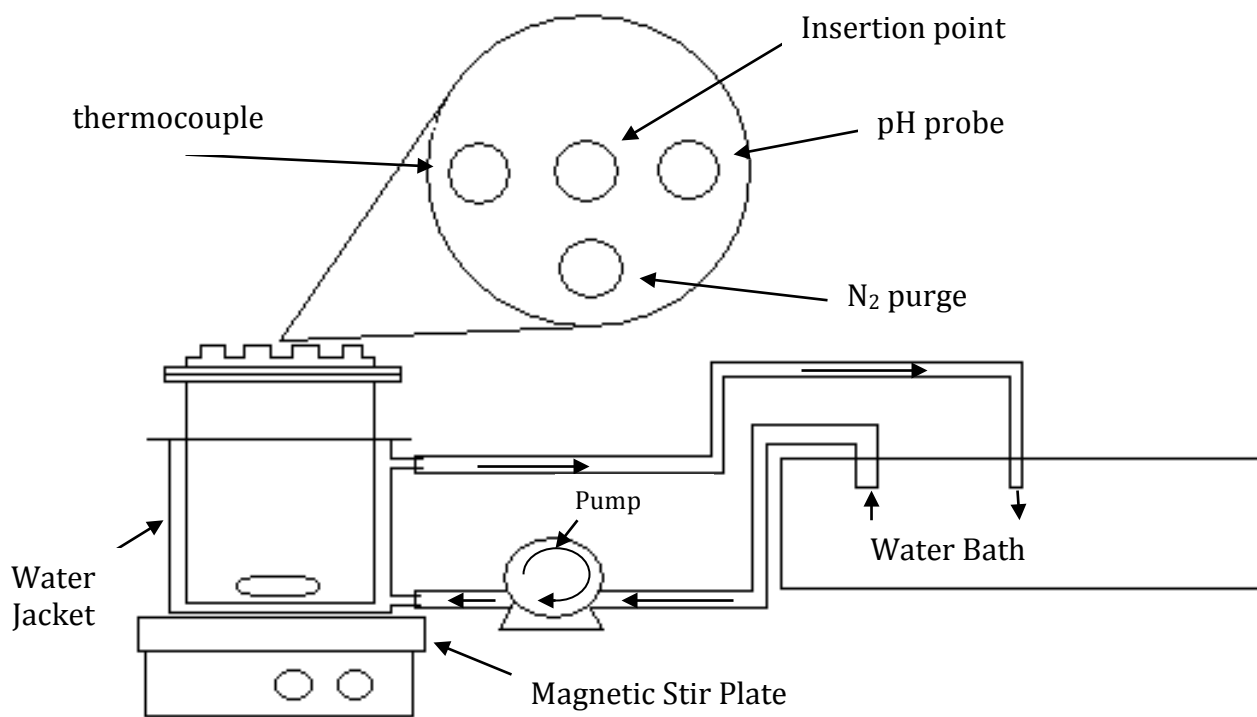
### **3.3 Methods**

#### **3.3.1 Batch Experiment**

A typical batch experiment involved the use of a one liter reaction flask with a cover containing four 24/40 joints. The flask was surrounded by a water jacket, and the four openings in the cover contained a pH probe, thermocouple, nitrogen line to purge any oxygen in the headspace, and an insertion point for raw primary sludge. The digester was stirred using a magnetic stir bar. A schematic of the apparatus can be found in Figure 3.1.

**Table 3.1 Tested range during parametric analysis**

<b>Parameter</b>	<b>Range of Test</b>
pH	5.5 – 8.0
Temperature	30, 35, 40, and 55°C
Alkalinity	1,500 – 2,500 mg/L as CaCO <sub>3</sub>
Volatile Fatty Acid Content	300 – 6,400 mg/L HAc



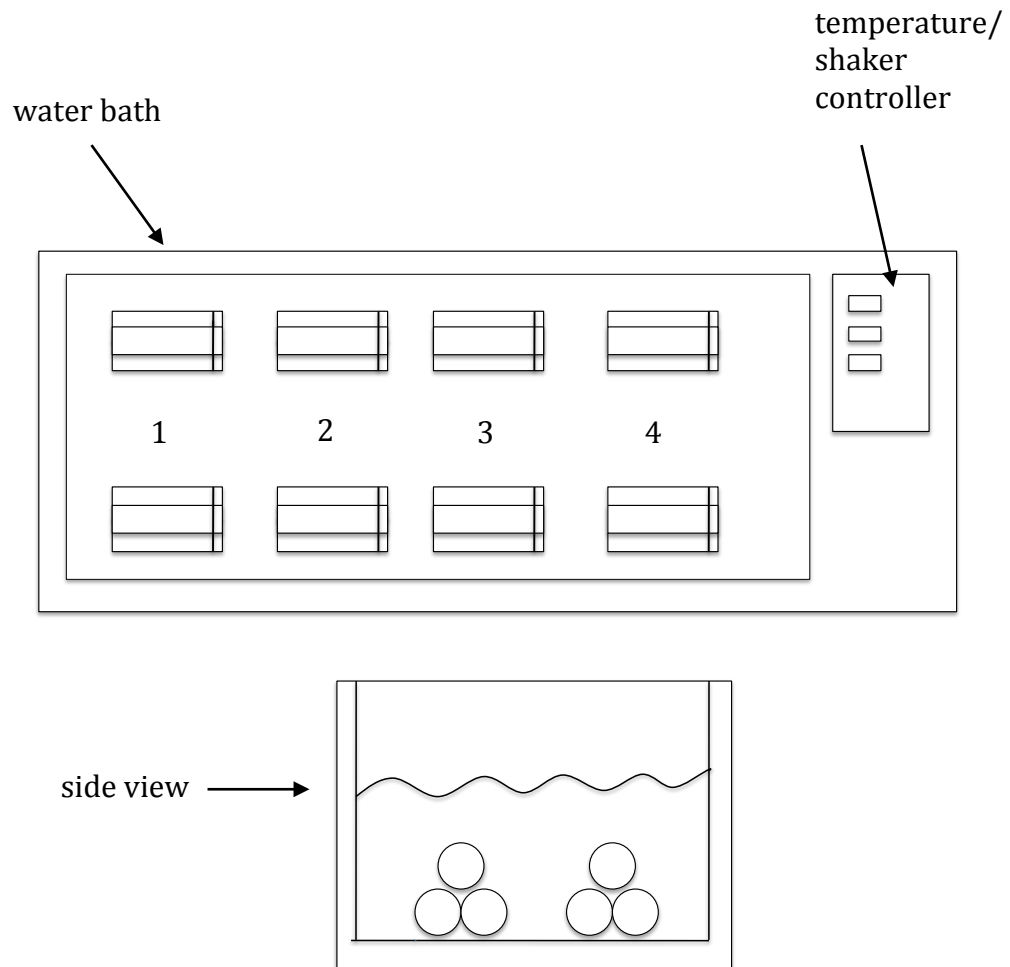
**Figure 3.1 Schematic of experimental batch system**

To begin testing, approximately one liter of partially digested primary sludge was put into the reaction flask and allowed to come to temperature ( $35 \pm 1^{\circ}\text{C}$ ), where it was maintained for the entire experiment. An Orion 5-star meter was used to measure pH every fifteen minutes with a ROSS combination electrode. This measurement would continue for the entirety of the experiment, lasting between 15–30 days. The system was closed off from the outside environment with rubber septa, and nitrogen was used to purge the system when open to the outside environment.

After pH measurements were taken to establish the initial portion of the pH curve, the system was opened for the addition of forty milliliters of raw primary sludge. This amount coincides with a twenty-five day retention time for a 1-liter reactor, consistent with HFWWTP operations. The nitrogen line was turned on once the system was opened, and remained on until the flask was sealed. Once raw primary sludge was added, the insertion port was sealed using a rubber septum. An initial gas sample taken from the reactor headspace using a syringe was analyzed using gas chromatography. Gas samples (24 cc) were taken daily to measure gas quality. The length of the experiment varied each time, lasting between 15-30 days.

### **3.3.2 Parametric Studies**

All parametric studies involved the adjustment of a single parameter at a time, with all other parameters held constant. Parametric studies were conducted in 40 mL sample vials, and were heated in a constant temperature bath ( $35 \pm 1^{\circ}\text{C}$ ) as shown in Figure 3.2. A



**Figure 3.2 Schematic of typical parametric testing setup**

typical experiment began by adding WAS (150 mL) to an Erlenmeyer flask for mixing with chemicals and raw primary sludge. Parameter adjustment would either occur before raw primary sludge had been added or after, as described in the sections below. Raw primary sludge was added based upon a 25-day retention time (6 mL), as seen above during batch trials. All additions were made using a graduated disposable pipet. Mixing of the solutions was done by hand using a stir rod. After the mixture was prepared, 30 mL would be added to each sample vial. The headspace of each sample vial would then be evacuated using a syringe (12 cc), creating a slight vacuum by clearing the headspace twice (24 cc). Nitrogen (10 cc) would then be added to maintain an anaerobic environment. The vials were placed into the water bath and were shaken at 135 rpm for the entire experiment (approximately 8–10 days). The shaker was only stopped to take gas samples. Stoppage time was approximately 15 minutes each day.

Gas samples were taken from each sample vial in each of the four test cycles shown in Figure 3.2. The make-up of each test cycle was identical, with each containing the entire tested range of the parameter along with repeat samples. The difference between cycles was the date for sampling. Typically, gas samples would be taken from cycle one vials on day 2 or day 3 of testing. The increment between the other cycles would vary from one day to three days. Therefore, the progress in gas production could be tracked over a number of days. All gas samples were analyzed using gas chromatography. Additional specifications for each parametric study are given below.

### **3.3.2.1 pH**

Raw primary sludge was added to the Erlenmeyer flask prior to adjustment with 1.0 N HCl or 1.0 N NaHCO<sub>3</sub>. Test cycles were set up with eight sample vials, including the pH values listed in Table 3.1 in increments of 0.5, a repeat at pH 7, and a control sample. The experiment lasted a period of ten days, and was conducted as described in section 3.3.2.

### **3.3.2.2 Alkalinity**

The alkalinity of a control sample of WAS was determined using the procedure described in Appendix A (EPA-430/9-77-006/March 1977). After the alkalinity of the control sample was determined, it was altered using 15.0 N Mg(OH)<sub>2</sub> and 0.1 N H<sub>2</sub>SO<sub>4</sub>. For example, each 30 mL sample would contain either 0.6 mL of 15.0 N Mg(OH)<sub>2</sub> or 4 mL of 0.1 N H<sub>2</sub>SO<sub>4</sub>. Raw primary sludge was then added to the Erlenmeyer flask corresponding to a 25-day retention time (6 mL). This mixture was then put into sample vials to begin the test. Test cycles contained six vials, including the values listed in Table 3.1 in increments of 500 mg/L as CaCO<sub>3</sub>, along with a repeat of each, and were tested as described in section 3.3.2.

### **3.3.2.3 Temperature**

Parametric analysis of temperature was conducted at four different temperatures (Table 3.1). Most of these fall within the mesophilic range, while the highest represents the thermophilic range. Samples were mixed as in section 3.3.2, with no chemical adjustment. Only WAS and raw primary sludge were used for testing. Four samples were analyzed at each temperature, with each having the same make-up. One gas sample was taken at the

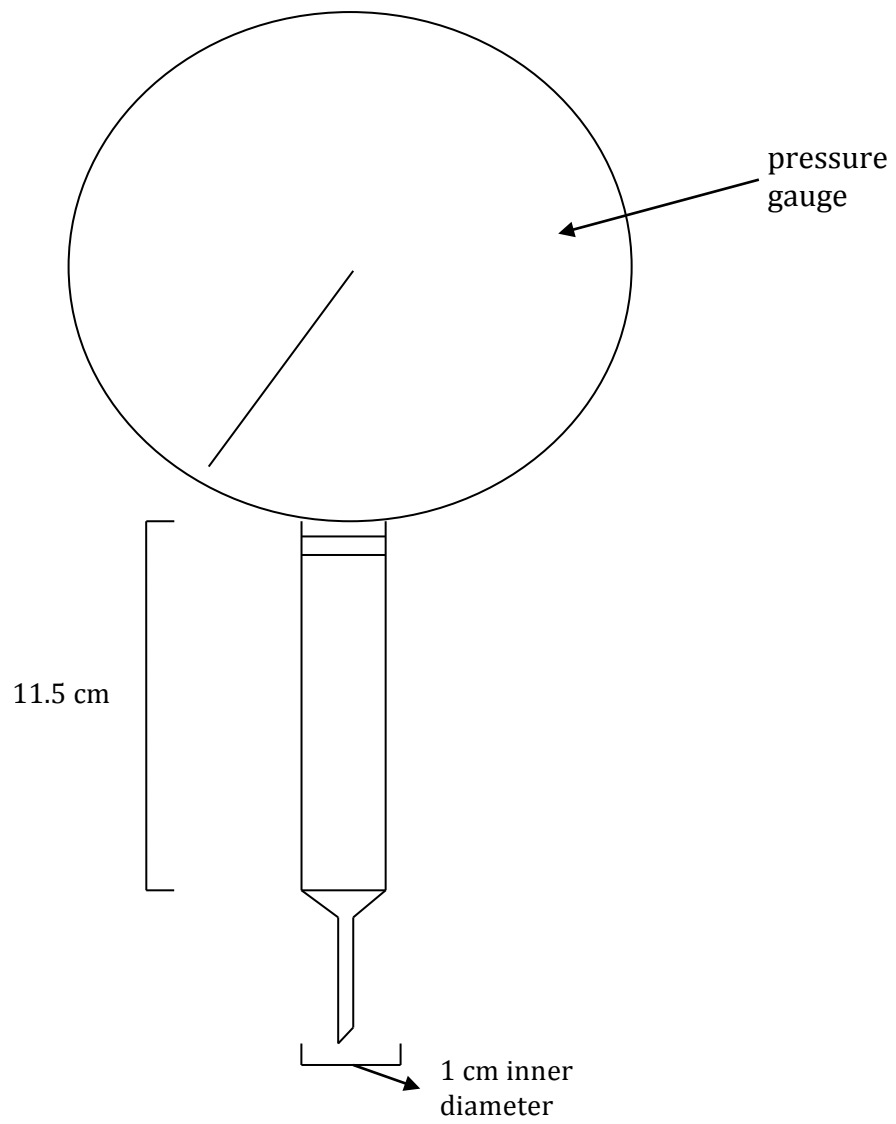
end of testing from each sample at each temperature. All tests lasted two days except for at 35°C, which lasted three.

#### **3.3.2.4 Volatile Fatty Acids**

The volatile fatty acid content of a control sample of WAS was determined using the procedure described in Appendix A (EPA-430/9-77-006/March 1977). For the first experiment, nine samples were tested with the following additions of 1.0 M sodium propionate solution for every 30 mL of WAS/raw primary mix: 0, 2, 4, 6, 8, 10, and 12 mL, with 6 and 12 mL samples being repeated for accuracy. A second test was performed using 10.0 M sodium propionate to test for the effects of dilution. Higher concentration sodium propionate reduced the required additions for every 30 mL of WAS/raw primary mix to: 0, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 mL, with 0.6 and 1.2 mL samples being repeated. After chemical adjustment, raw primary sludge was added corresponding to a 25-day retention time (1.2 mL). Test cycles for both experiments included the nine samples described above, and were tested as described in section 3.3.2.

#### **3.3.2.5 Pressure**

The pressure of each sample was determined during parametric analysis of VFA content. The apparatus used for testing can be seen in Figure 3.3. Using a pressure gauge attached to a 21-gauge needle through a piece of 11.5 cm tubing (1 cm inside diameter), the pressure of each vial was measured for gas production calculations using the ideal gas law. The increased volume of the testing apparatus was accounted for in all calculations. Pressure testing was completed prior to GC analysis.



**Figure 3.3 Pressure testing apparatus**

### 3.3.3 Semi-continuous Experiment

A typical semi-continuous experiment involved a similar experimental setup as previous batch experiments (Figure 3.1). However, digested sludge was removed and raw primary sludge was added on a daily basis. The raw primary sludge used for additions was at 6 °C. The parameters discussed in sections 3.3.2.1 – 3.3.2.4 were tested for a one week period. Parameter testing did not occur on a continuous basis in order to maintain a tight seal on the unit to accurately measure gas production. A balloon was used to capture all produced gas, and the amount collected was measured by water displacement.

In a typical experiment, the reaction flask was filled with 600 mL of WAS and allowed to come to temperature ( $35 \pm 1^\circ\text{C}$ ). Raw primary sludge was then added to the flask corresponding to a 25-day retention time on a daily basis (24 mL). An equal volume of digested sludge was removed from the system prior to the addition of raw primary sludge. The reactor volume was tested for pH and temperature on a daily basis as additions were being made, and VFA content and alkalinity were tested every other day during the experiment. VFA content and alkalinity measurements of the collected digest were determined using the procedures found in Appendix A. When VFA and alkalinity measurements were made, 60 mL of digest were collected, therefore lowering the total volume of the reactor as well as the amount of raw primary sludge added daily.

A control experiment was set up similar to control samples used during parametric studies (section 3.3.2). A mixture of WAS and raw primary sludge (30 mL) was put into sample vials and allowed to run unchanged for a one week period. The control reaction was allowed to operate without adjustment of the parameters in question, and temperature

was held constant at  $35 \pm 1^{\circ}\text{C}$ . This setup resembled a batch system, but was used in comparison to previous control samples to determine if the sample obtained from HFWWTP for semi-continuous testing produced similar results to previous sludge samples retrieved from the plant. Analysis of gas samples taken from both of these systems was done using GC.

### **3.4 Analytical Methods**

#### **3.4.1 Gas Chromatography**

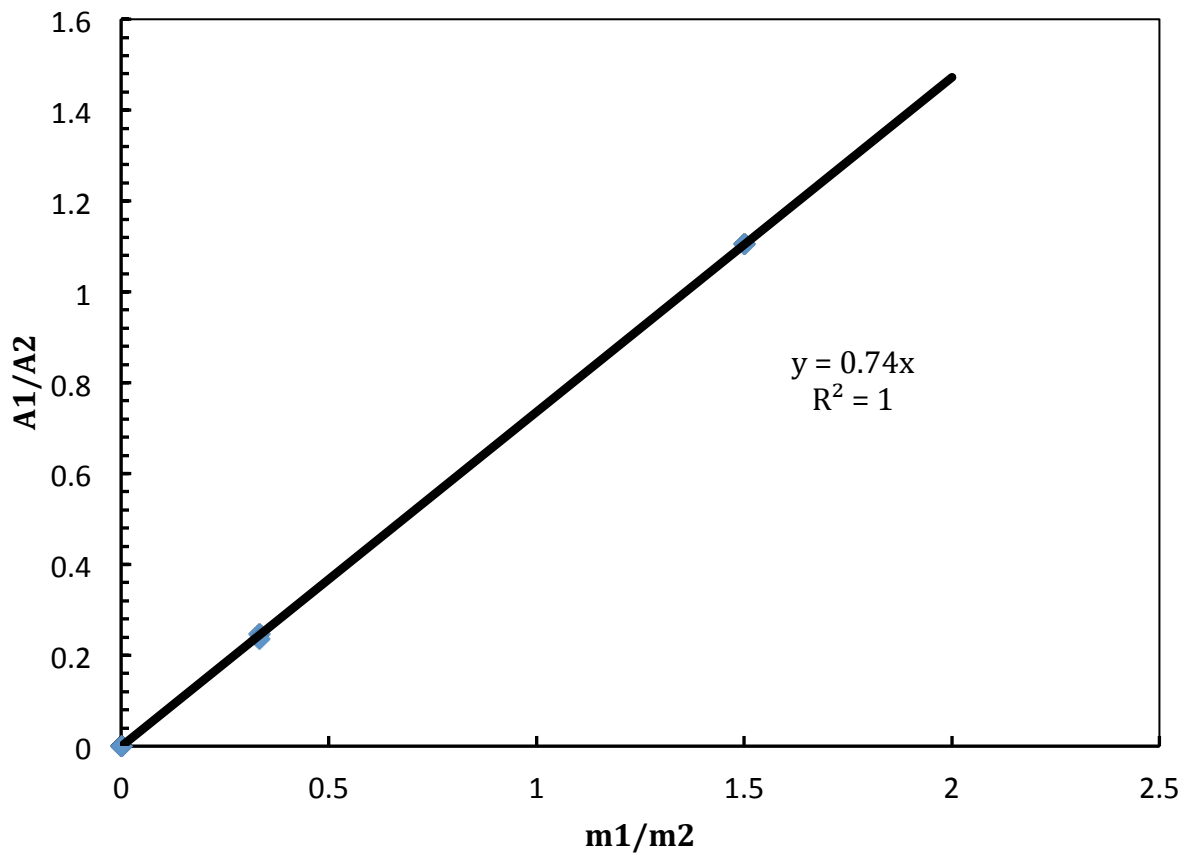
A Shimadzu GC-14A gas chromatograph (GC) equipped with a packed column and a Valco Instruments Co., Inc. (VICI) actuator valve was used to analyze all gas samples. The solid support of the column was 80/100 Porapak Q spherical beads, classified as the least polar commercially available porous polymer [55]. The column measured  $3 \text{ m} \times \frac{1}{8} \text{ in.}$  Helium was used as the carrier gas (250 scc/min) and a TCD detector was utilized for the output signal. The elution time for each sample was 1 minute. The oven temperature was held at  $50^{\circ}\text{C}$  while the detector was held constant at  $90^{\circ}\text{C}$ . The VICI actuator valve has a 1 mL loop that fills with gas upon sample insertion. The gas contained within the loop is displaced by the inserted sample. The sample continues to flow through the loop, pushing excess sample out the exit of the loop, ensuring that the sample loop only contains 1 mL for consistent sample size. Once the run is started, the loop closes, pushing the sample into the column for analysis. One end of the line leading to the loop contained a rubber septum and the other was immersed in water to ensure no air could interfere with sample analysis.

Each gas sample was taken from the headspace of the reacting vessel. Syringes (12 cc) were used to extract each sample. When doing batch experiments, 24 cc of gas were taken from the headspace of the reaction flask for GC analysis. When running parameter analysis experiments, only 12 cc of gas were extracted from the headspace of the sample vials. These samples would then be pushed through the sample loop on the actuator valve, leading to GC analysis. To ensure that a previous sample would not affect the GC analysis of the current sample during parametric analysis, 12 cc of nitrogen were pushed through the loop prior to the sample being inserted, in essence to purge the loop. Once the samples had been processed, percent area read-outs would be used, along with a calibration curve, to determine the amount of methane in each sample.

### **3.4.2 Gas Chromatography Calibration Curves**

#### **3.4.2.1 Methane Concentration**

To determine the quality of the produced gas, known mixtures of methane and carbon dioxide were analyzed using gas chromatography. The following ratios (mole%) of methane to carbon dioxide were used: 0:100, 25:75, 60.01:39.99, and 100:0. Figure 3.4 shows the calibration curve for methane. Only the areas of methane (A1) and carbon dioxide (A2) peaks were used for the curve. The parameter  $m1$  represents the known concentration of methane and  $m2$  is represented by the formula  $m2 = 100 - m1$ . The parameters  $m1$  and  $m2$  have units of mole%. An error of  $\pm 0.5$  mole% is expected when using this curve, based on the standard deviation of curve areas for methane and carbon dioxide.



**Figure 3.4** Calculated methane concentration calibration curve

### **3.4.2.2 Gas Production Rate**

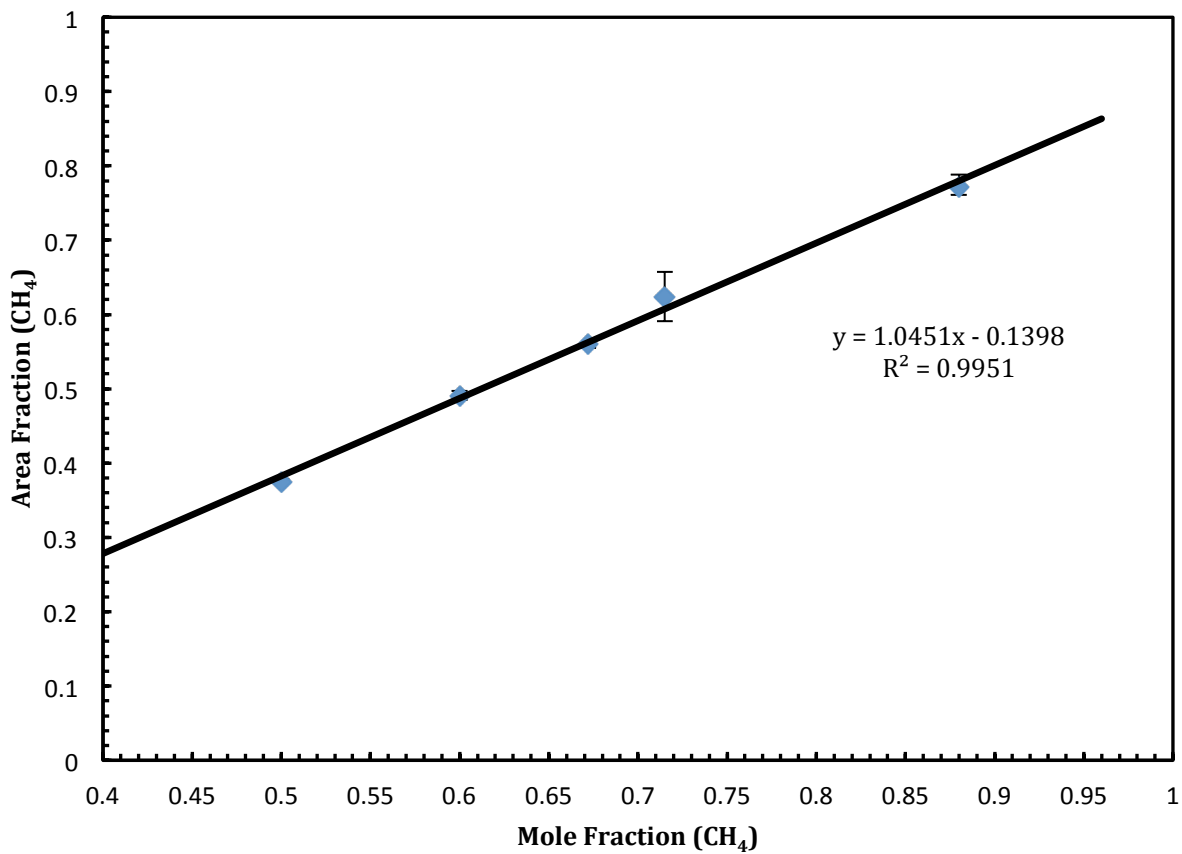
Known amounts of nitrogen, methane, and carbon dioxide were inserted into a sample vial and then extracted for GC analysis to determine the amount of biogas being formed during parametric studies. To begin, the vials were filled with 30 mL of water similar to parametric testing. The headspace of the vial was evacuated using a syringe to make sure no gas was contained inside that might affect GC analysis. After this, the three gases were inserted in known amounts, allowed time to mix, and then analyzed. This was repeated each time a new configuration was tested and each gas configuration was done in triplicate. Table 3.2 shows the amounts of each gas from each test, and Figure 3.5 shows the calibration curve. The area fraction on the y-axis is calculated from GC analysis, leading to the determination of the mole fraction of CH<sub>4</sub> within the system. Both area fraction and mole fraction include nitrogen. Typical error with this curve is  $\pm 2$  mole%, based upon the average error of five known samples.

### **3.4.3 Hilliard-Fletcher Wastewater Treatment Plant Testing**

Before and after each batch experiment, a 200 mL sample of digested sludge was transported to the HFWWTP for testing. Analysis of the sample determined the following: total solids (%), volatile solids (%), pH, alkalinity (mg/L as CaCO<sub>3</sub>), and volatile acids (mg/L as HAc). This was done in order to examine the differences in pre- and post-digest samples. This collaboration also allowed for expanded testing of samples beyond the capabilities of our laboratory. Alkalinity and volatile acids measurements were done using EPA-430/9-77-006/March 1977 as in our laboratory, and total solids and volatile solids were tested using Standard Methods 2540D and 2540E (19<sup>th</sup> ed.), respectively.

**Table 3.2 Known amounts of gas used for calibration of production rate**

<b>Sample</b>	<b>Nitrogen (mmol)</b>	<b>Methane (mmol)</b>	<b>Carbon Dioxide (mmol)</b>
1	0.42	0.839	0.42
2	0.42	1.26	0.42
3	0.42	1.68	0.42
4	0.336	1.68	0.336
5	0.084	2.5	0.252



**Figure 3.5 Mole fraction calibration of CH<sub>4</sub> for production rate data**

## CHAPTER FOUR RESULTS & DISCUSSION

### 4.1 Introduction

This chapter presents the results of extensive experiments involved with improving the production rate of biogas formed through the anaerobic digestion of sewage sludge. Efforts have been made with each experiment to better understand the digestion process in order to correlate a change in the production rate with the corresponding parametric adjustment. Changes were made to pH, temperature, alkalinity, and volatile fatty acid content. The hypothesis of this research is that optimization of the parameters of the anaerobic digestion of sewage sludge will lead to an increase in the production of biogas.

### 4.2 Digester Energy Balance

It was determined that the HFWWTP digesters require  $1,022.5 \frac{m^3}{day}$  CH<sub>4</sub> to maintain a temperature of 35°C at atmospheric pressure. Based on a ratio of 60:40 (methane to carbon dioxide) biogas, each digester will require  $1,705 \frac{m^3}{day}$  biogas at those same conditions. Scaling parametric results to plant operations at the HFWWTP showed the ability to provide  $1,944 \frac{m^3}{day}$  biogas at the highest capacity, based on a 1 million gallon digester. At lower production, parametric studies produced  $718 \frac{m^3}{day}$  biogas. Samples tested during parametric studies regularly produced biogas nearing 80% methane. By increasing the methane content of produced biogas from 60 to 80%, the heating value of the gas increases

by one-third. These numbers clearly show that optimization of the digestion process can dramatically enhance the quantity and quality of produced biogas, therefore requiring less volume of gas for plant operation. This provides the opportunity for higher energy efficiency, as fewer outside energy sources would be necessary for plant operation. The complete calculations for this energy balance can be found in Appendix B. Assumptions for these calculations include complete combustion and 80% boiler efficiency. Calculations for the energy balance were based upon the addition and removal of  $276,600 \frac{lb \text{ sludge}}{day}$  from each digester (average operation at the HFWWTP). All gas volumes are reported at atmospheric pressure and a temperature of 35°C.

### **4.3 Batch Experimentation with pH Analysis**

#### **4.3.1 Monitoring with pH**

The purpose of batch testing was to gain a better understanding of the digestion process. The digest was used as received from the HFWWTP, and no other additions were made after the initial inoculation with raw primary sludge. Microorganisms in the initial inoculum were allowed to feed upon the partially digested sludge, and the process was monitored through continuous recording of pH. Each of the three curves seen in Figure 4.1 represents one batch experiment. Batch experiments are time dependent, and therefore the observed variations in pH were expected. By contrast, digesters at the HFWWTP are operated continuously in steady state, and the system pH is relatively constant.

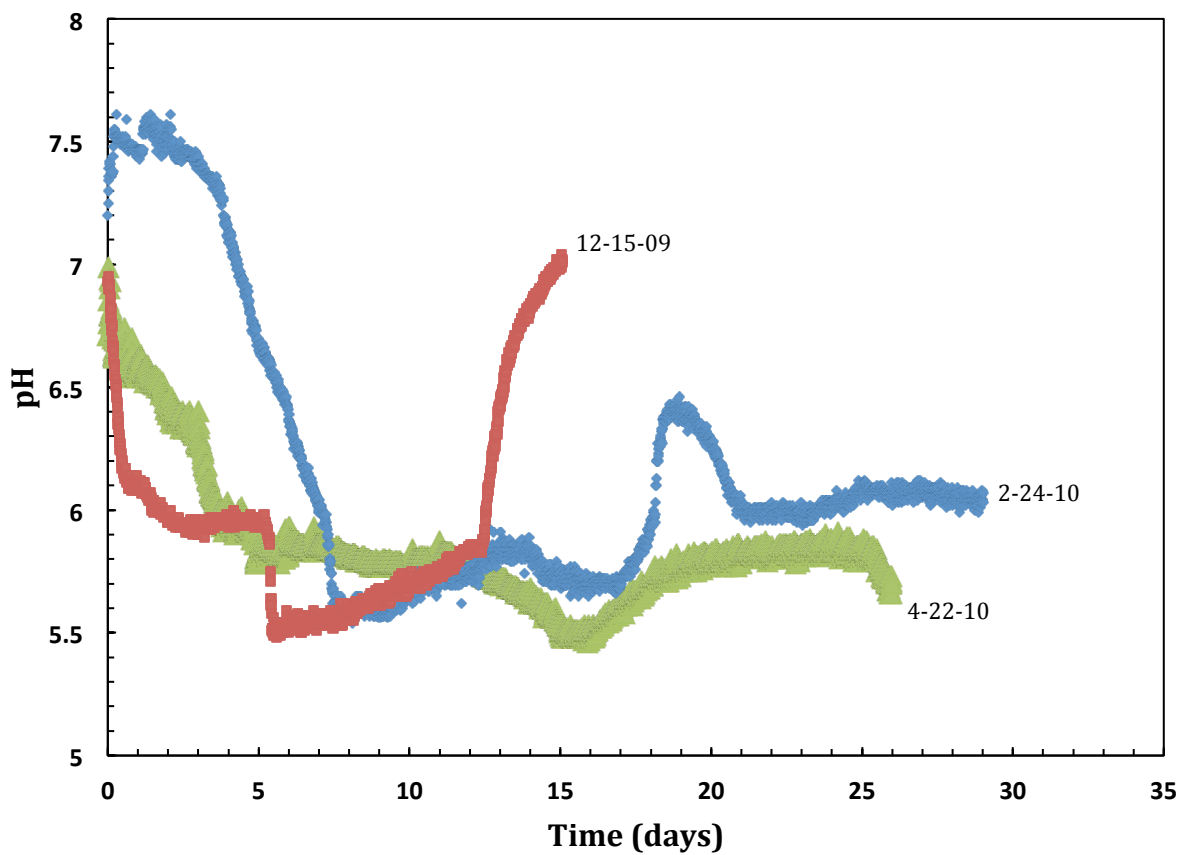


Figure 4.1 pH monitoring during batch experimentation

The inoculation with raw primary sludge was only done once per experiment, providing an initial amount of microorganisms between the inoculate and the partially digested sludge already in the digester. The microorganisms break down the sludge and multiply causing changes in digester conditions, which were tracked through changes in pH. Initially, a quick drop in pH was observed, followed by a period of pH stability, and finally an upswing in the last portion of the experiment.

The initial drop in pH was caused by an increase in acid content. Extensive hydrolysis and acidogenesis over the first 5-7 days in all three experiments resulted in acidification of the digest. The pH of the digest held relatively constant over the following 5-10 days, and was most likely dominated by acetogenesis. The difference between acidogenesis and acetogenesis is the change in acid end products. The end products of acidogenesis are hydrogen and VFAs, composed of butyric, propionic, and acetic acids. Acetic acid makes up approximately 60% of the end products of acidogenesis, while hydrogen and the other VFAs, as a whole, make up roughly 20% each [33].

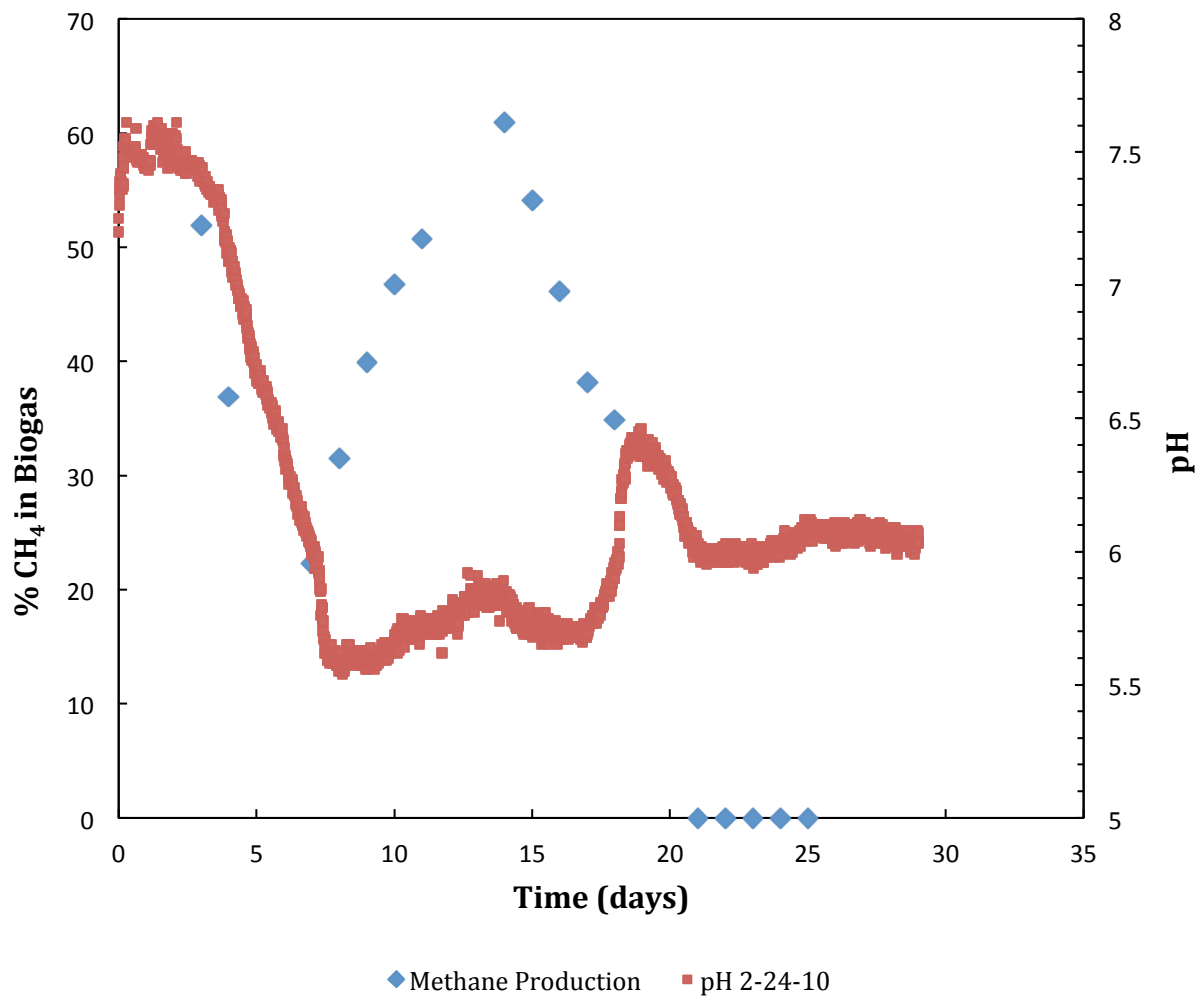
During acetogenesis, the remaining VFAs are broken down into acetic acid. The observed variations in pH during acetogenesis were most likely due to the different products formed from the breakdown of butyric and propionic acids. When one mole of butyric acid is digested, two moles of acetic acid are formed along with two moles of hydrogen (Figure 2.2). A corresponding decrease in pH would occur as two moles of acid replace one mole of acid. The breakdown of propionic acid gives one mole each of acetic acid and carbon dioxide, along with three moles of hydrogen. The result would be an increase in pH due to the increased buffering capability of the system with the added

carbon dioxide. The experimental results in Figure 4.1 did not show large variations in the fermentation stage, and therefore the amounts of butyric and propionic acids present at the beginning of acetogenesis were similar.

After fermentation, the pH began to rise, signifying that the acid concentration of the digest had decreased. The rise in pH was due to the formation of carbon dioxide and methane from the breakdown of acetic acid. An increase in CO<sub>2</sub> concentration within the digest increases the alkalinity due to the carbon dioxide/bicarbonate equilibrium. With a smaller amount of acids available for methanogenic bacteria to digest, methane formation began to decline, signaling an end to digestion.

#### **4.3.2 Acetogenesis and Methanogenesis**

The data in Figure 4.2 verified that acetogenesis and methanogenesis occurred simultaneously. This graph shows the methane concentration of the produced biogas and the pH of the digest as functions of time. The amount of methane being produced initially decreased during hydrolysis, but increased during fermentation. The initial drop in methane formation may be due to an increase in digester acid content, which inhibited methanogenic activity. The subsequent rise in methane content shows that acids were simultaneously formed and broken down. While the pH of the digest was not typical for promotion of methanogen activity, the rise in methane content in the produced biogas shows the ability of the methanogens to adjust and buffer the environment. The methane production did not continue to rise though as the pH rose, showing that the acid content within the digester was depleted.

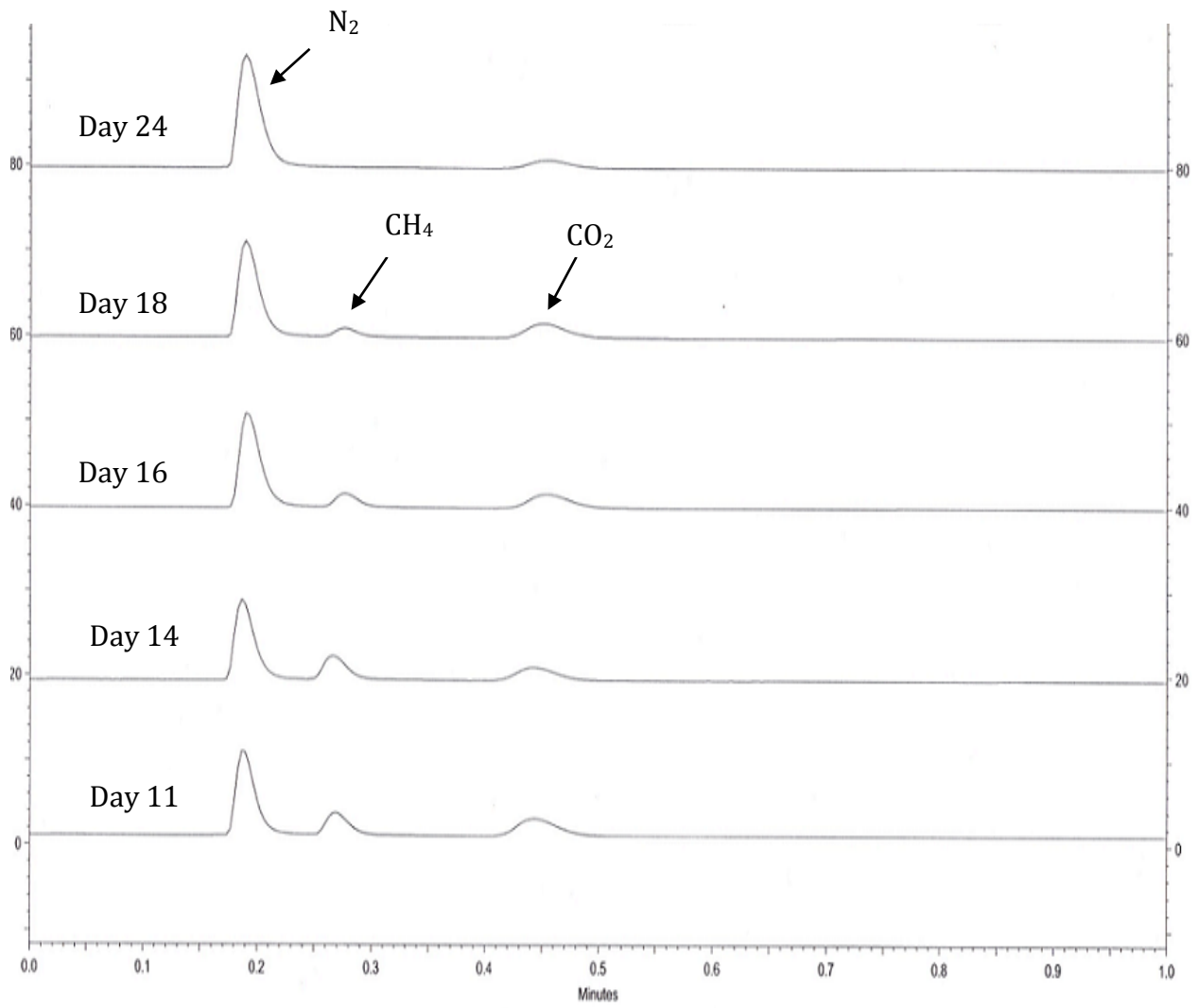


**Figure 4.2 Methane concentration and pH as a function of time**

Figure 4.3 shows sequential chromatograms from analyzed gas samples throughout the second batch experiment, each showing a peak for nitrogen, methane, and carbon dioxide. The bottom chromatogram was taken on day 11, while the top chromatogram was taken on day 24. The nitrogen peak did not diminish throughout the experiment, while the methane and carbon dioxide peaks changed greatly. Given that 24 cc of sample were removed each time a sample was analyzed, there is the possibility that a slight vacuum was pulled on the digester, allowing air to be pulled into the system. This would allow for the first peak to remain large, as air and pure nitrogen give no differences in GC analysis. Since gas samples were being removed from the reactor, the amount of methane within the reaction vessel was depleted on a daily basis. The amount of methane being formed decreased as the amount of acids decreased, and therefore the concentration of methane within the gas samples began to decrease after day 14 (Figures 4.2 and 4.3). This continued until the methane peak was no longer visible. After day 21 (Figure 4.2), all methane had been removed from the system through sampling, and no methane was being formed.

#### **4.3.3 End of Digest Observation**

An observation noticed during batch testing was the difference in the final stage of the pH curves in Figure 4.1. In the initial batch digest, the curve began to move upward and continued to ascend until the test was stopped. The test was stopped at the end of 15 days because the high pH indicated that the digestion process was complete. It was expected that each of the digests would finish with a neutral pH, similar to that of the first batch experiment, but neither of the subsequent batch tests rose above pH 6.5. Both



**Figure 4.3 Sequential chromatograms of produced biogas**

experienced a period where the pH began to rise, but neither maintained the upward ascent. The contradiction here is that the only mechanism for the pH to remain low would be an increase in the acid content. Since methanogenic activity had ceased within the last two digests, represented by no methane content in biogas samples, it was assumed that there was a low acid content within the digester, as acetogenesis and methanogenesis occur simultaneously. Testing upon these latter two digests at HFWWTP showed the alkalinity of both digests to be above 3,400 mg/L CaCO<sub>3</sub> and VFA content to be above 300 mg/L HAc. The alkalinity of the digests falls within the expected range discussed in section 2.5.3, but the VFA content of the digest was higher than expected for values found in the literature. A healthy digester should have a low VFA content, usually below 200 mg/L HAc [42]. The higher quantity of VFAs present in the digest would create a high hydrogen partial pressure, greatly affecting the performance of the methanogenic bacteria and causing the digester to “sour”.

#### **4.3.4 Reduction of Solids**

Anaerobic digestion has long been used as an effective method for reducing solids within the wastewater treatment process. Table 4.1 shows results from HFWWTP testing upon a sample of raw primary sludge and a digested sample, both used during batch tests. The substantial drop in solids from the raw sample to the digested sample verified the effectiveness of anaerobic digestion for reduction of solids. Volatile solids are organic material that can be decomposed, and therefore the digested sample had potential for further digestion. However, when the digest was allowed to run for one week after all methanogen activity had ceased, no additional breakdown of volatile solids was observed.

**Table 4.1 Reduced solids during batch testing**

<b>Digest 2 (2/24/2010)</b>	<b>Raw Primary Sludge</b>	<b>Digested Sludge</b>
Temperature (°C)	35	35
Total Solids	6.93%	1.64%
Volatile Solids	2.71% of total	0.984% of total
Alkalinity (mg/L as CaCO <sub>3</sub> )	1,160	3,560
pH	5.75	7.63
VFA (mg/L as HAc)	295	385

Differences in sample alkalinity and pH were also noted. The low alkalinity and pH of the raw sample indicated an excess of acids, and were most likely responsible for the quick drop in pH shown in Figure 4.1 from each of the batch tests. Table 4.1 represents only one sample of raw primary sludge obtained from HFWWTP, but test results throughout the batch experiments were similar, pointing to only small variations between obtained samples.

#### **4.4 Parametric Analysis**

Parametric analysis was used to determine the optimum range of the parameters pH, temperature, alkalinity, and VFA content. A fifth parameter, pressure, also showed an effect upon the digestion during parametric tests. Since parametric analysis was completed using sample vials, the system could be completely sealed, allowing the pressure to increase as biogas was produced. The effect of increased pressure was very evident in the amount of gas produced as well as the quality of the produced gas. Each parameter tested, along with pressure, will be discussed below with experimental evidence as to the optimum operating range for anaerobic digestion.

##### **4.4.1 pH**

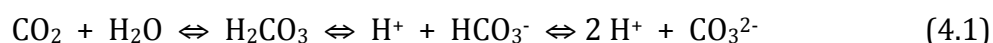
The pH of an anaerobic digester can be influenced by many factors. Batch testing data (Figure 4.1) showed that pH can fluctuate greatly throughout the digestion process. The main factors affecting the pH of a digest are alkalinity and acid content. If the acid content of a digester is too high, the system pH drops resulting in reduced methanogenic activity and decreased gas production. This example shows how vital pH is to the monitoring of digester activity. The pH of a digest is an indicator of the current phase of

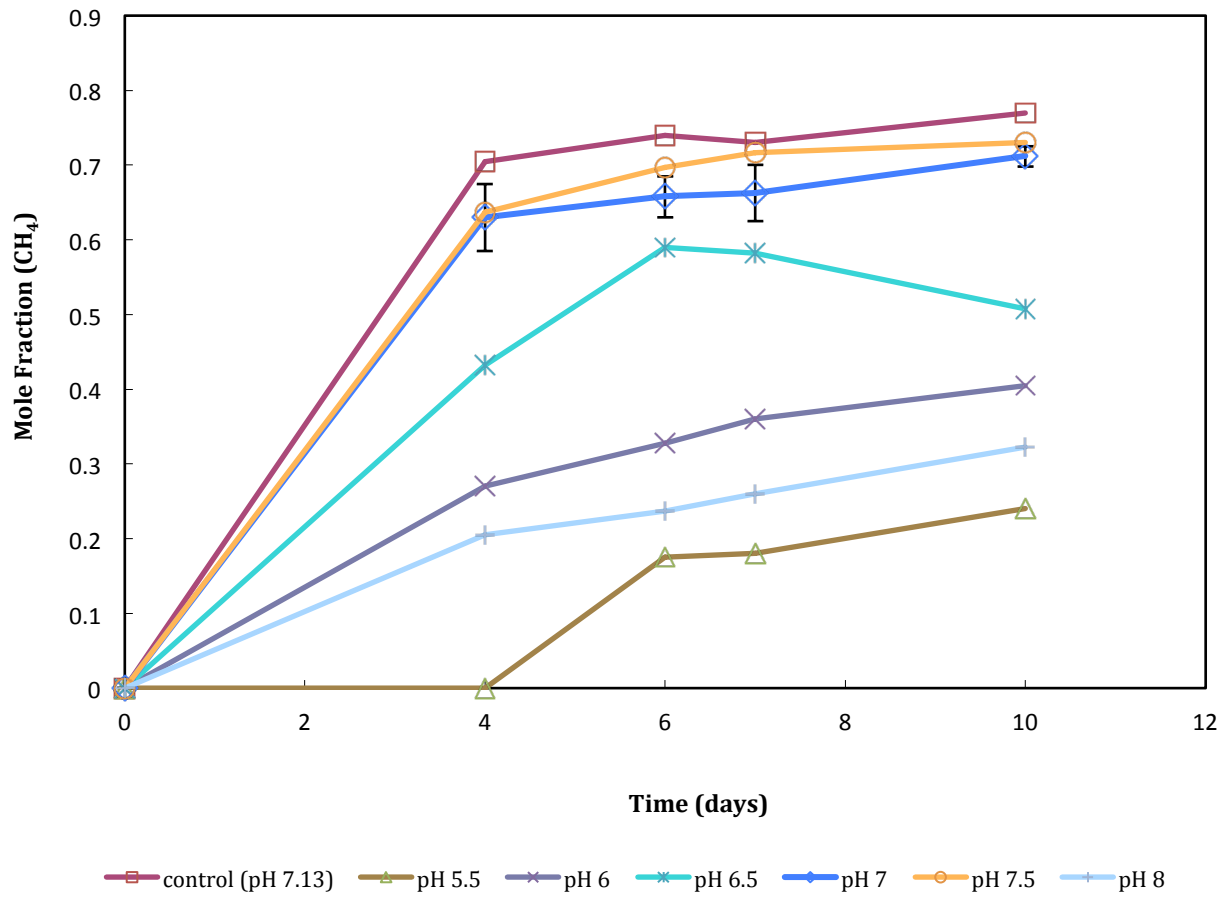
digestion, and can be used to determine if there is a build-up of acid in continuous experiments. It therefore serves as a diagnostic parameter to determine actions required to maintain the digestion process.

Figure 4.4 shows the mole fraction of produced methane as a function of time. The samples shown in the figure are represented by the initial pH of the digest. Since each sample vial was a closed batch system, the pH could not be monitored throughout the test and it was not known if the pH remained constant. However, based on the data in Table 4.2, final pH measurements for each of the vial samples did not vary greatly in most cases. As expected, methanogenic activity rapidly decreased outside of a neutral pH range. The control sample began at pH 7.13 and had the highest mole fraction of methane throughout the experiment. The two samples closest to the control sample, pH 7.0 and pH 7.5, showed similarly high methane mole fractions throughout the experiment. The accepted pH range for maximum methanogenic activity varies among researchers, but in general a neutral pH ranging from 6.8 – 7.2 is thought to be best [12]. The results shown in Figure 4.4 agree with this, showing the highest mole fraction of methane produced in samples beginning near a neutral pH. These three samples represent the optimum pH range for gas production, pH 7.0-7.5.

#### 4.4.2 Alkalinity

Methanogens depend upon their ability to buffer the digestion system in order to operate effectively. Equation 4.1 shows the equilibrium between carbon dioxide and bicarbonate.





**Figure 4.4 Parametric results for pH testing**

**Table 4.2 Comparison of pH values before and after testing**

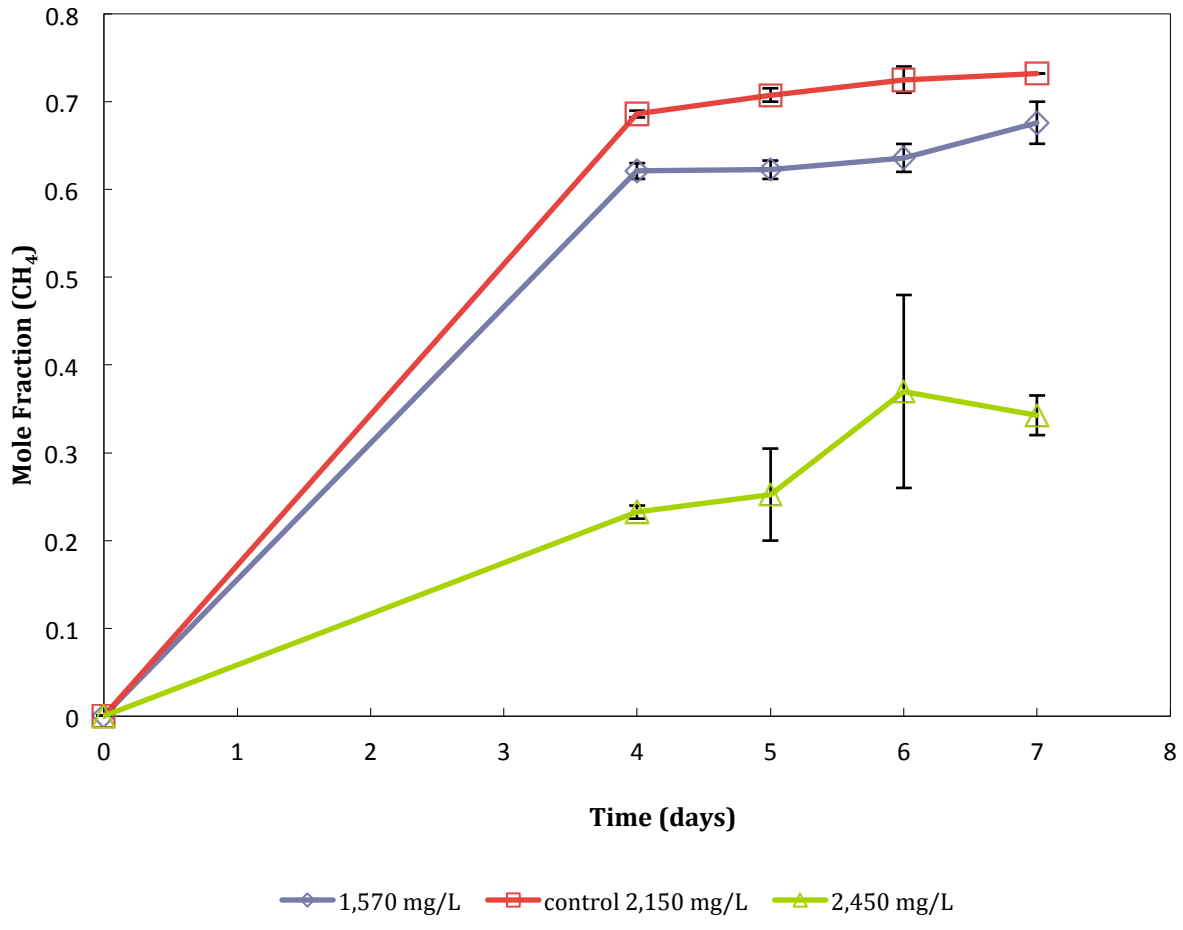
<b>Sample</b>	<b>Initial</b>	<b>Final (day 10)</b>
Control	7.13	$7.03 \pm 0.2$
1	5.5	$5.91 \pm 0.14$
2	6.0	$6.30 \pm 0.03$
3	6.5	$6.53 \pm 0.09$
4	7.0	$6.91 \pm 0.03$
5	7.5	$7.28 \pm 0.01$
6	8.0	$7.78 \pm 0.03$

This equilibrium allows methanogens to buffer the digestion process to counteract an increase in the acidity of the digest. When carbon dioxide is released, the production of carbonic acid and bicarbonate ensues. Alkalinity can be in the form of ammonia or carbon dioxide, but is reported as calcium carbonate. A similar equilibrium to that seen with carbon dioxide exists between ammonia and ammonium (Equation 4.2).



Since testing upon the supernatant (Appendix A) does not explicitly give the source of the alkalinity, it was determined that the source was from the equilibrium between  $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ . This is based upon the titration of the sample to pH 4 during alkalinity testing. The equilibrium between carbonic acid and bicarbonate has a  $\text{pK}_a$  of 6.4, while the  $\text{pK}_a$  values for ammonia/ammonium and carbonate/bicarbonate are both above 9. Therefore, there is a much greater chance for the system to be buffered by  $\text{H}_2\text{CO}_3/\text{HCO}_3^-$  than other systems.

The results shown in Figure 4.5 offer a contrast to those seen in the literature [42]. Typical alkalinity values for a healthy digest range from 4,000-5,000 mg/L as  $\text{CaCO}_3$ . Literature values typically represent a continuous system, and therefore may not be completely relevant for batch parametric studies. Figure 4.5 shows the highest mole fraction of methane was achieved with the control sample, which began at 2,150 mg/L as  $\text{CaCO}_3$ . Sample 1,570 produced similar values for  $\text{CH}_4$  mole fraction, while sample 2,450 produced well below the other samples. Since sample 2,450 began with the highest alkalinity, it was expected to have the highest gas production out of the three alkalinities tested. An explanation for this low gas production can be seen in Table 4.3, which shows



**Figure 4.5 Mole fraction of produced methane during parametric analysis of alkalinity**

**Table 4.3 Parametric results from the testing of alkalinity**

Sample	Initial (mg/L as CaCO <sub>3</sub> )	Final (mg/L as CaCO <sub>3</sub> )	Final pH
Control	2,150	2,500 ± 50	7.69
1,570	1,570	2,140 ± 65	7.6
2,450	2,450	2,775 ± 125	9.26

the initial and final alkalinities, as well as the final pH, of the three samples. Although the initial pH of the system was not tested, the final pH of each sample was indicative of the low methane production of sample 2,450. The final pH of each sample was outside of the optimum pH range established in previous parametric studies, but sample 2,450 was much higher than the other samples, which were just outside the optimum range. The pH of sample 2,450 was not conducive to methane production [17]. This was most likely the result of using magnesium hydroxide to raise the alkalinity, instead of a source of carbonate. Magnesium hydroxide was used here because it is used at the HFWWTP for the same purpose. It causes a rise in both alkalinity and pH, most likely due to dissociation, which causes two moles of hydroxide to be released into solution. Therefore, sample 2,450 might have been doomed from the beginning of testing by the use of  $Mg(OH)_2$ . The use of a carbonate or bicarbonate would have raised the alkalinity of the solution by creating a sink for  $H^+$ , but not making the pH shoot upward due to the equilibrium between carbonic acid and bicarbonate having a  $pK_a$  of 6.4.

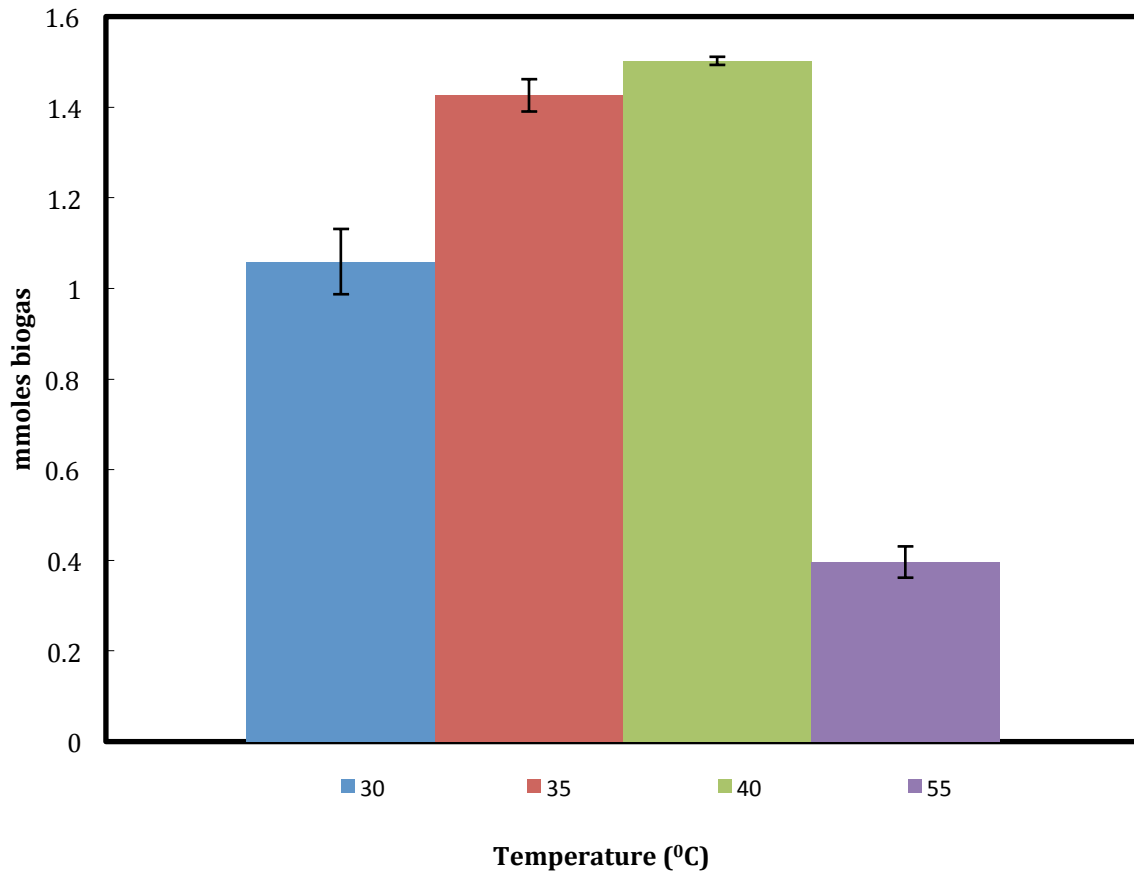
It is difficult to determine the optimum range of alkalinity based upon the testing methods used during parametric studies. By chemically altering the alkalinity, the digestion process was disrupted, which could delay the response of the microorganisms within the system. These additions caused poor balance between system parameters, and bacteria had to adjust before normal operation continued. In the case of alkalinity, it seems as though the microorganisms in sample 1,570 recovered faster from this disruption than those in sample 2,450. Given time to respond, sample 2,450 may have shown a similar production to that of the other two samples, but this was doubtful due to the high final pH of the sample. Comparing Figure 4.5 and Table 4.3, it seems as though the optimum range of

alkalinity falls between 2,000-2,500 mg/L CaCO<sub>3</sub>, but this cannot be concluded due to testing procedures of this parametric study.

### **4.4.3 Temperature**

#### **4.4.3.1 Mesophilic Range Differences**

Temperature tests were run in order to determine differences in biogas production within the mesophilic range and at a thermophilic temperature of 55°C. The data in Figure 4.6 show total production of biogas at each tested temperature. The experiment at 35°C ran for 3 days, while the others ran for 2 days. Samples tested at 40°C produced the most gas, averaging over 1.5 mmoles of biogas per sample. Assuming that the daily production rate at each temperature was similar, the first two temperatures tested (30 and 35°C) produced similar amounts of biogas. In order to make a determination for the optimum temperature within the mesophilic range, the amount of energy used to heat the samples and maintain the set temperature of each sample was needed. Simple calculations were made to estimate the energy needed to heat 30 mL of sludge to 40°C and 30°C. Based upon the parametric study apparatus with a room temperature of 20°C, the amount of energy needed to heat and maintain at 40°C (2.9 kJ) was double that required at 30°C (1.44 kJ). Calculating the energy value of the produced biogas for each sample, 0.5 kJ were formed at 40°C and 0.45 kJ were formed at 30°C. The amount of outside energy, other than biogas, needed to heat the sample to 40°C was double that required at 30°C. Therefore, operation within the lower part of the mesophilic range would be more energy efficient.



**Figure 4.6 Parametric testing upon different temperatures within the mesophilic and thermophilic ranges**

#### 4.4.3.2 Mesophilic and Thermophilic Comparison

Samples tested within the mesophilic range produced on average 0.93 mmoles of biogas more than samples tested at the thermophilic range (Figure 4.6). Following literature, thermophilic bacteria should reproduce faster while also reducing retention times when comparing to mesophilic bacteria. The advantage of mesophilic bacteria is their stability throughout the mesophilic range [22]. Data shown in Figure 4.6 supports the second of these claims, showing higher production throughout the entire mesophilic range than that within the thermophilic range. The most likely cause of the low production seen in the thermophilic sample seems to be related to characteristics of thermophilic bacteria. These bacteria lack the diversity associated with mesophilic anaerobes and have a high endogenous death rate, causing inconsistent treatment of sludge during digestion [17]. A second explanation could be a low concentration of thermophilic bacteria within the digest.

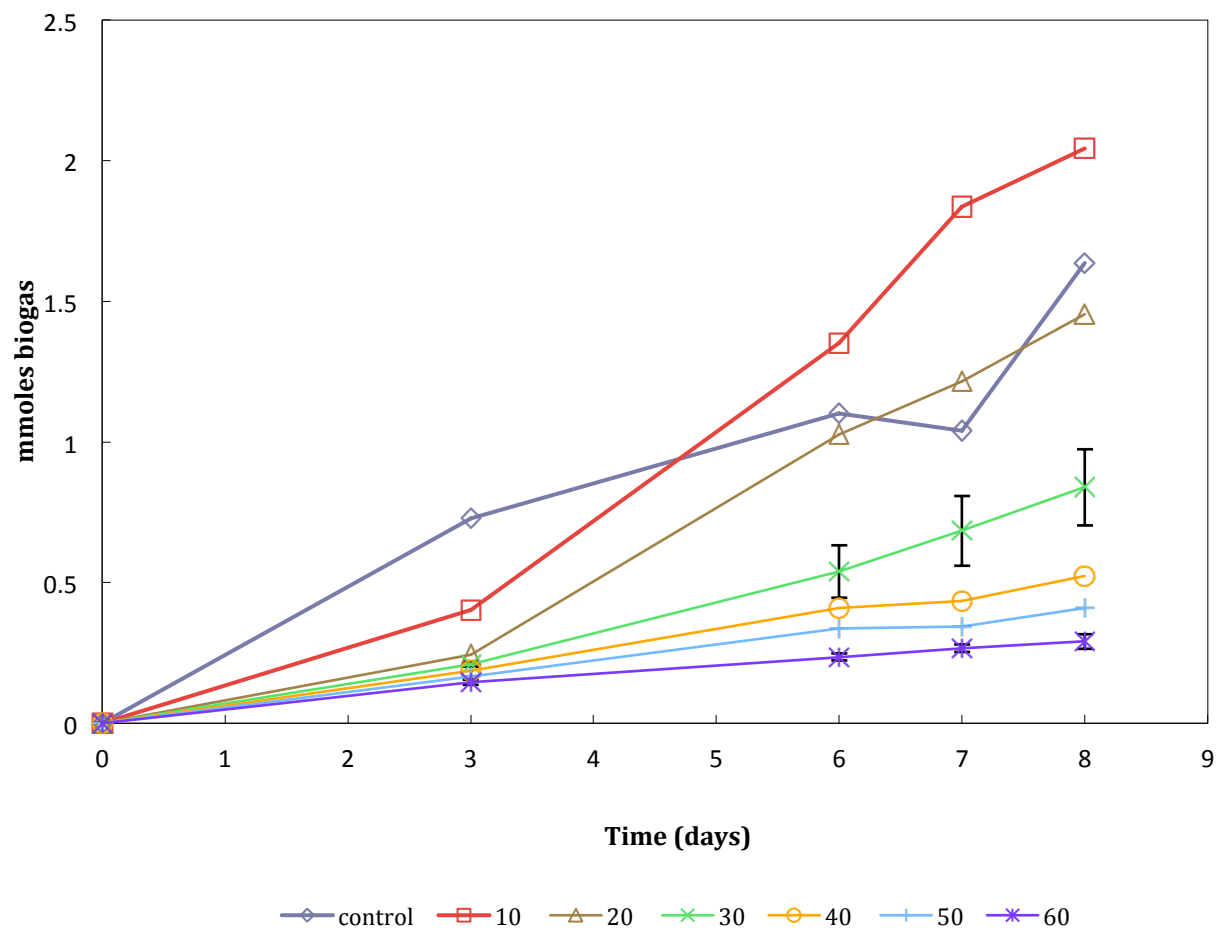
Stepping back to the discussion of energy requirements for heating the constant temperature bath, it is known that the amount of energy needed to heat water to 55°C is more than that needed for 40°C. Since the biogas production at 55°C falls well below that observed throughout the mesophilic range, the use of biogas as a replacement energy source would not be plausible at thermophilic temperatures based on Figure 4.6. If anaerobic digestion does not produce enough biogas for use as an energy source, then a major benefit for its use has been lost. Therefore, it can be concluded that anaerobic digestion operated at mesophilic temperatures provides optimum production over temperatures within the thermophilic range.

#### 4.4.4 Volatile Fatty Acid Content

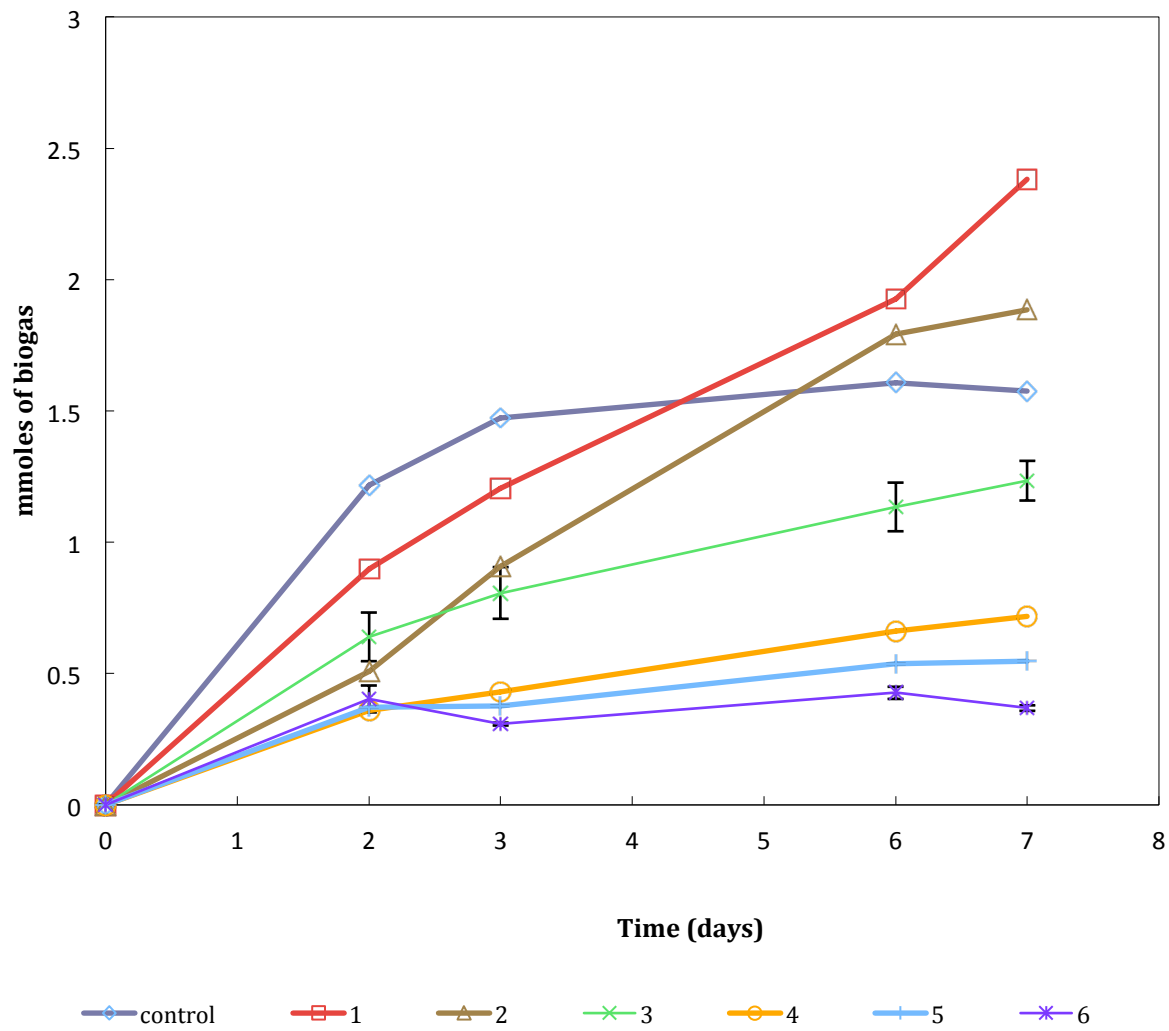
Tests to examine the effects caused by volatile fatty acids upon the anaerobic digestion of sewage sludge produced mixed results. As seen in Figures 4.7 and 4.8, doping the system with sodium propionate greatly affected the digestion process. At high initial levels of added VFA, the digestion process struggled to recover. When small adjustments were made, as in samples 10 and 1 in Figures 4.7 and 4.8, respectively, the production of biogas outperformed the control at longer times.

Figure 4.7 shows data based on the addition of 1.0 M sodium propionate. The control sample began with a high production of biogas, but was bypassed by sample 10 five days after the experiment began. All other samples showed lower production of biogas when compared to the control sample. The initial slow period for sample 10 was likely caused by the addition of excess VFAs, causing a shock to the methanogens. This was quickly overcome by the methanogen ability to buffer the system through the equilibrium between carbon dioxide and bicarbonate. The increased amount of VFAs within the digest provided more substrate for consumption by acetogenic and methanogenic bacteria. This was also seen in Figure 4.8 as the production of biogas for sample 1 continued to rise at the end of the experiment while the control sample began to plateau after just three days.

The results in Figure 4.7 also show that the buffering capability of methanogens was not strong enough to overcome the addition of large doses of excess VFAs. In most cases, tested samples with larger amounts of VFAs took twice as long to create similar amounts of biogas as sample 10. The only other sample remotely close to sample 10 in terms of production was sample 20, averaging over 0.4 mmoles of biogas less than sample 10 at



**Figure 4.7 Results from initial parametric study upon VFA content**

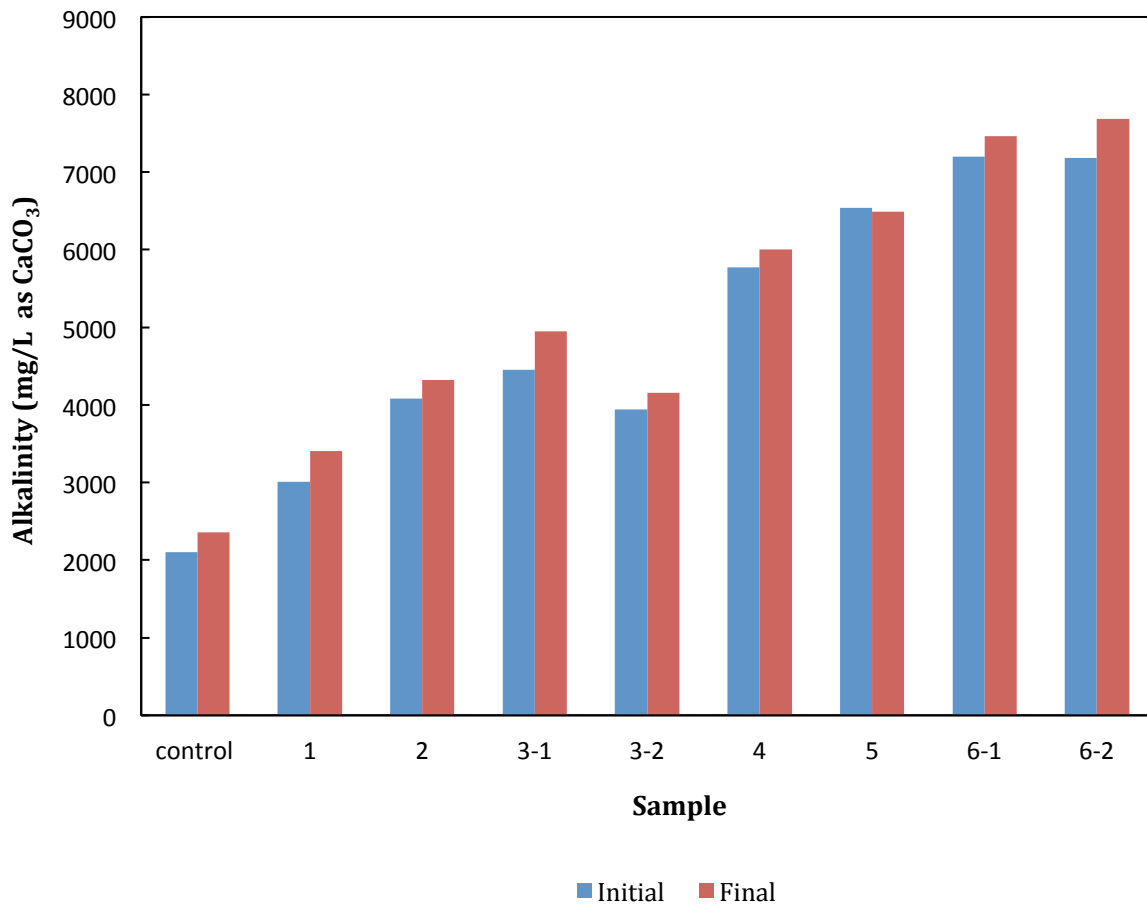


**Figure 4.8 Results from parametric study of VFA content testing dilution effects**

each testing. With large amounts of VFAs present in the digest, the hydrogen partial pressure was high, negatively affecting acetotrophic methanogens. When the breakdown of acetic acid by methanogens was slowed, the digestion process began to shut down due to end-product inhibition of the fermentation stage.

VFA experiments were repeated using a higher concentration solution of sodium propionate to examine the effects of dilution. As shown in Figure 4.8, the results were similar to the first experiment, with a noticeable increase in gas production in similar samples from Figures 4.7 and 4.8, i.e. 10 and 1, 20 and 2, etc. This difference in production could be attributed to the dilution of samples with lower concentration sodium propionate. By diluting the samples with large amounts of 1.0 M sodium propionate, in some cases one-third of the sample, smaller amounts of microorganisms and sludge were in each sample for digestion. This may have lowered the ability of each sample to produce biogas. Therefore, sample dilution can cause a reduction in the ability of a sample to produce biogas.

The addition of sodium propionate to each digest not only increased the VFA content, but also the solution alkalinity, as seen in Figure 4.9, which shows all tested samples from the study of dilutional effect on VFA content. By definition, alkalinity is the acid neutralizing capacity of an aqueous solution [52]. By adding sodium propionate to the solution instead of propionic acid, a hydrogen sink was added, increasing the alkalinity of the solution. The test used for measuring alkalinity (Appendix A) was a titration method. The added propionate acted as a  $H^+$  sink as the solution was titrated, resulting in an increase in solution alkalinity. The pH of the tested supernatant during alkalinity testing



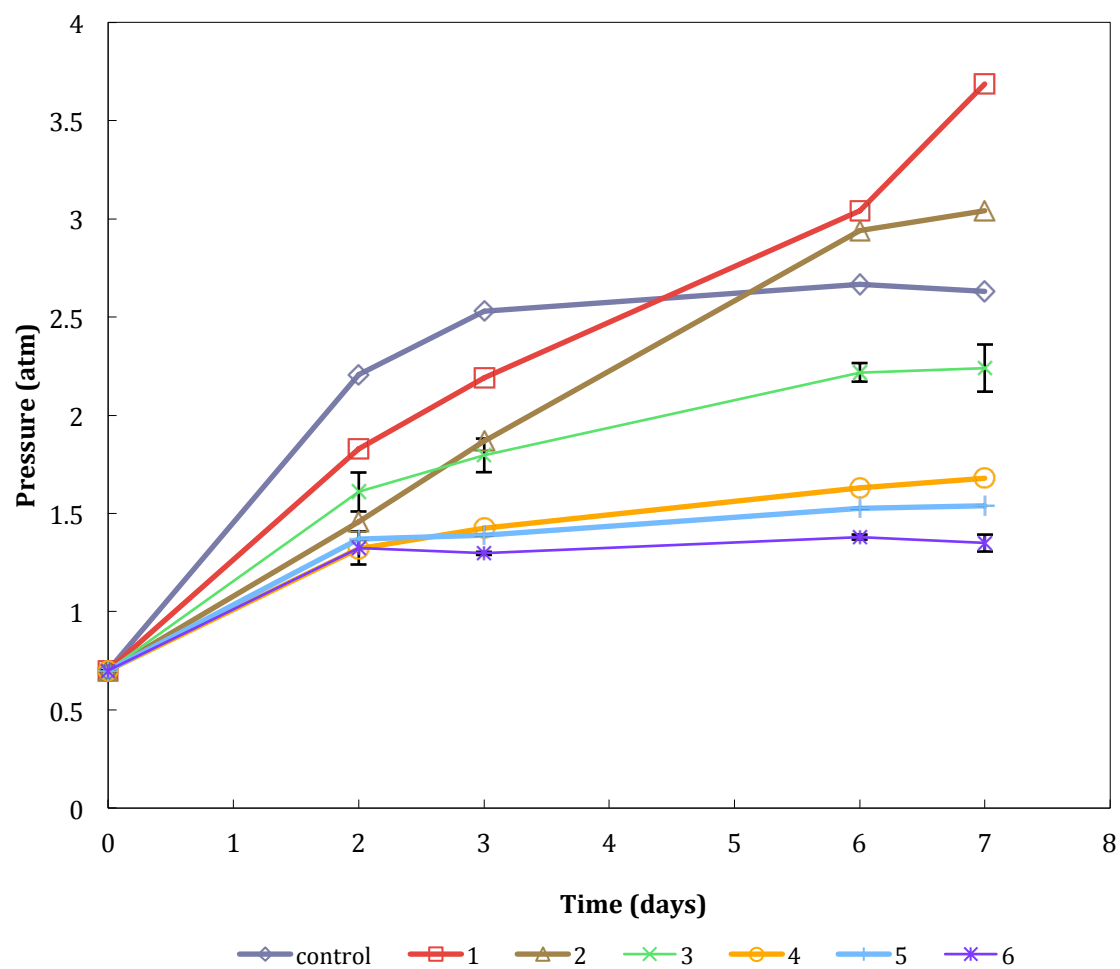
**Figure 4.9 Initial and final alkalinity measurements during parametric study of VFA content**

was consistently around 7.5. The rise in alkalinity that occurred after the addition of sodium propionate also gives credence to the argument that magnesium hydroxide was a poor choice for raising alkalinity during parametric study of alkalinity. Consequently, the observed increase in biogas production over the control sample may be due to the simultaneous increase in VFA content and alkalinity. The latter helps to keep the system stable so that the methanogens can continue to function and continue breaking down the formed acids.

#### **4.4.5 Pressure Effects**

It was observed that sample pressure increased during all of the parametric studies. The pressure increase was due to increased biogas production. In addition, the pressure increase and the amount of gas produced were highest at optimum pH. Similar results were observed for alkalinity and VFA content. This can be seen in Figures 4.8 and 4.10 as pressure was explicitly measured during VFA parametric studies. Figure 4.10 shows the pressure as measured during adjustment with 10 M sodium propionate.

The gas production within the sample vials was apparent due to stretching of the septum. The build-up of biogas in the sample vials caused the pressure to increase. Pressure was measured so that the molar production rate could be determined from the Ideal Gas Law. The pressure of each sample vial was measured using a pressure gauge attached to a 21-gauge needle before the gas sample was taken for GC analysis. The data in Figure 4.10 show a significant pressure increase for all samples, with each sample beginning slightly under atmospheric pressure after the headspace was evacuated and nitrogen was added. The samples in Figure 4.10 correspond to the samples in Figure 4.8. In

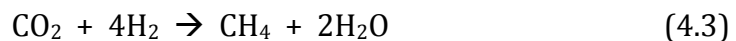


**Figure 4.10 Pressure measured during adjustment of VFA content with 10 M sodium propionate**

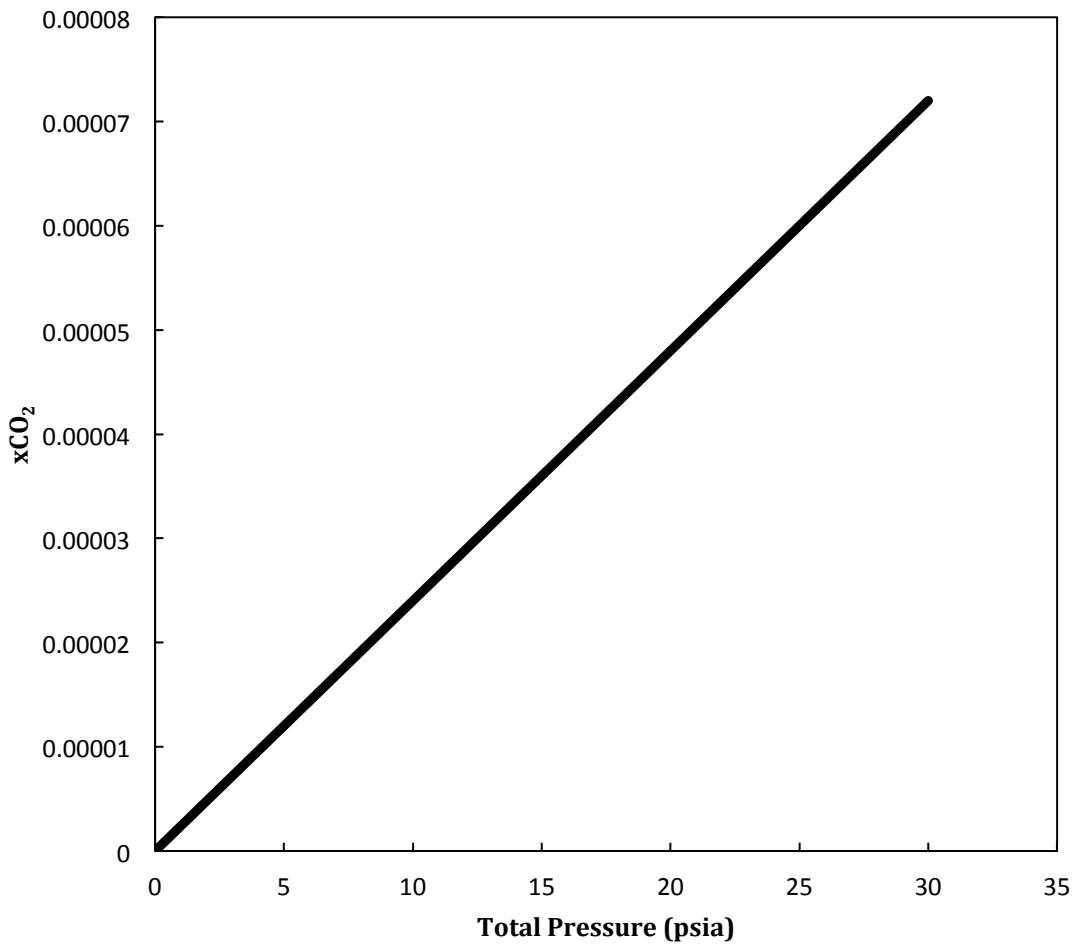
one case, sample 1, the pressure was still increasing after seven days. This showed that biogas production was not yet complete. By contrast, pressure plateaued after only three days for the control sample.

A second observation for these results was the similarities of the curves for Figures 4.8 and 4.10. The biogas production curve for each sample in Figure 4.8 was nearly identical to the corresponding pressure curve in Figure 4.10. This showed that gas production and pressure were dependent on each other, as an increase in biogas production caused an increase in system pressure. Likewise, an increase in pressure caused an increase in production. The latter was due to the VLE behavior of carbon dioxide and water. As the pressure increased within the system, carbon dioxide dissolved into the liquid phase, as it is soluble in water, resulting in increased methane formation.

Using ChemCAD, the VLE behavior of carbon dioxide and water was calculated (Figure 4.11) to determine how much carbon dioxide would be soluble in the liquid phase with increasing pressure. The data in Figure 4.11 shows a two-fold increase in CO<sub>2</sub> solubility when pressure increases from 15 to 30 psia. Methane has little solubility in water, and therefore would remain in the gas phase. Since carbon dioxide can be reduced by methanogenic bacteria, this additional carbon dioxide in the liquid phase would drive the reaction forward, creating more methane. The reaction is shown in Equation 4.3.



Therefore, more methane was formed through the reduction of carbon dioxide as more carbon dioxide dissolved into the liquid phase at higher pressure. This results in a much higher quantity and quality of biogas, which leads to higher heating values. The increase in



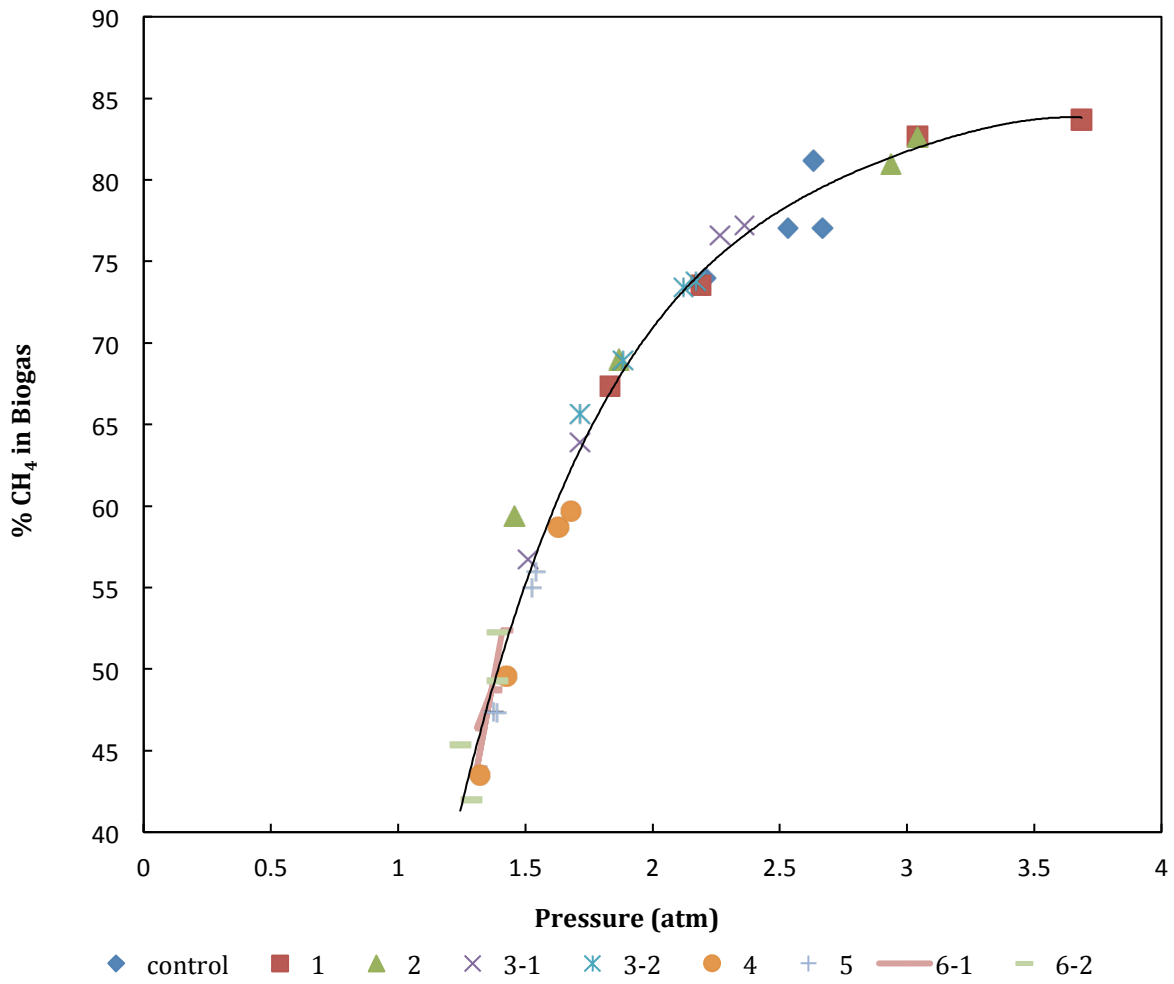
**Figure 4.11 Mole fraction of CO<sub>2</sub> within the liquid phase (ChemCAD)**

gas quality can be seen in Figure 4.12, which shows the % methane as a function of pressure measured during VFA parametric studies. This figure corresponds to the samples in Figure 4.8. As the pressure increased, the amount of methane within each sample increased until the trend plateaued at 85% methane. This was also noticed during parametric studies of pH and alkalinity, with the most productive samples ranging from 75 - 85% methane, much higher than the expected methane content of 60% [12,20].

As the pressure increased on the digestion system, the buffering capacity also increased due to a higher concentration of carbon dioxide in the liquid phase. Since methanogens depend on the ability to buffer changes in the system through the equilibrium between bicarbonate and carbon dioxide, an increase in carbon dioxide translates into a higher buffering capability within the reactor. Therefore, an increase in pressure not only increased gas production and quality, it also enhanced the ability of the system to buffer changes through the carbon dioxide/bicarbonate equilibrium.

#### **4.5 Semi-continuous Testing**

The semi-continuous system was constructed to test the optimum ranges provided by the parametric studies. To begin, each parameter was tested to determine an initial value from which adjustment could be made, if necessary. As shown in Table 4.4, the initial pH and temperature of the sludge were within the optimum range determined through parametric studies, but the alkalinity and VFA content were both lower than the optimum values determined during parametric studies. Knowing that the addition of sodium propionate increased both the alkalinity and VFA content of the vial samples, 4 mL of 10.0 M sodium propionate was added to the digest, bringing the alkalinity to 1,940 mg/L



**Figure 4.12 Increasing methane content with increasing pressure seen during adjustment of VFA content with 10 M sodium propionate**

**Table 4.4 Test results from semi-continuous experiment**

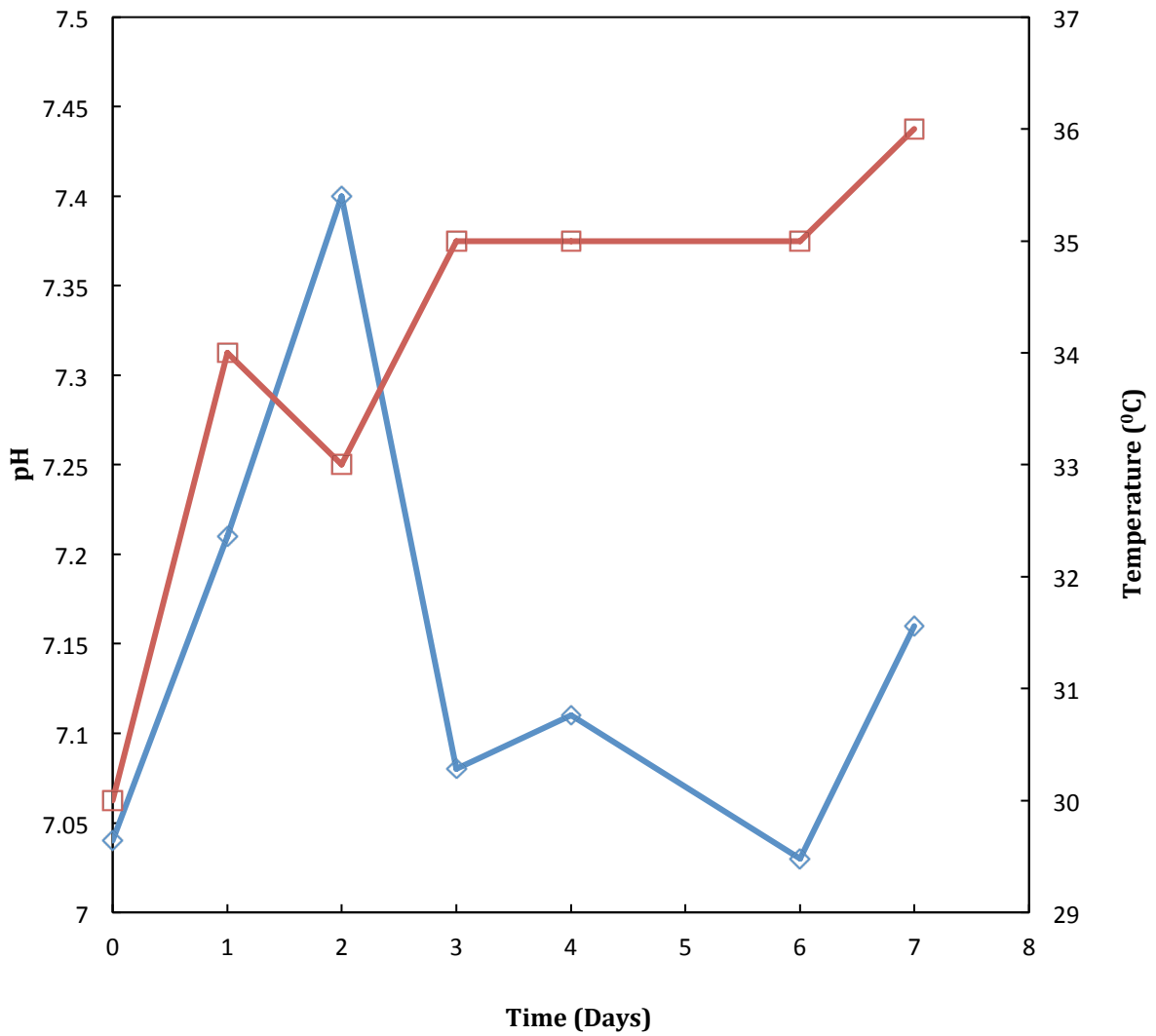
Day	pH	Temperature (°C)	Alkalinity (mg/L as CaCO <sub>3</sub> )	VFA content (mg/L as Hac)	Biogas Produced (cc)
Initial	7.04	30	1,200	245	0
Adjusted			1,940	1,250	
1	7.21	34			79
2	7.4	33	2,140	2,025	86
3	7.08	35			42
4	7.11	35	2,530	2,505	48
6	7.03	35	2,730	2,505	101
7	7.16	36			85

as  $\text{CaCO}_3$  and VFA content to 1,250 mg/L HAc. This amount of sodium propionate corresponded with the amount added to sample 1 in Figure 4.8. Once operation began, gas production was monitored on a daily basis to evaluate digester performance at optimized conditions.

#### **4.5.1 Parametric Monitoring**

Figure 4.13 shows that the pH and temperature fluctuate throughout testing within the optimized range for operation determined through parametric studies, showing the stability of these two parameters within the tested system. These parameters were measured only once per day in order to ensure that the reactor remained air-tight for maximum gas collection. Other than a jump to 7.4 on day 2, pH remained near neutral throughout the entire experiment. The stability of the pH during testing seems to be misleading due to the large amount of VFAs within the digest (Table 4.4). A higher acid content would tend to cause the pH to drop, but the use of sodium propionate instead of propionic acid as an additive balanced out the effect on the system pH by increasing the solution alkalinity.

Temperature was the one true independent variable throughout testing, as it was controlled by an external source. Therefore, any fluctuation in temperature was the result of external adjustment instead of internal activity within the system. There did not seem to be a direct link to a change in temperature affecting the biogas production, further cementing the argument that operation across the mesophilic temperature range should result in stable production.

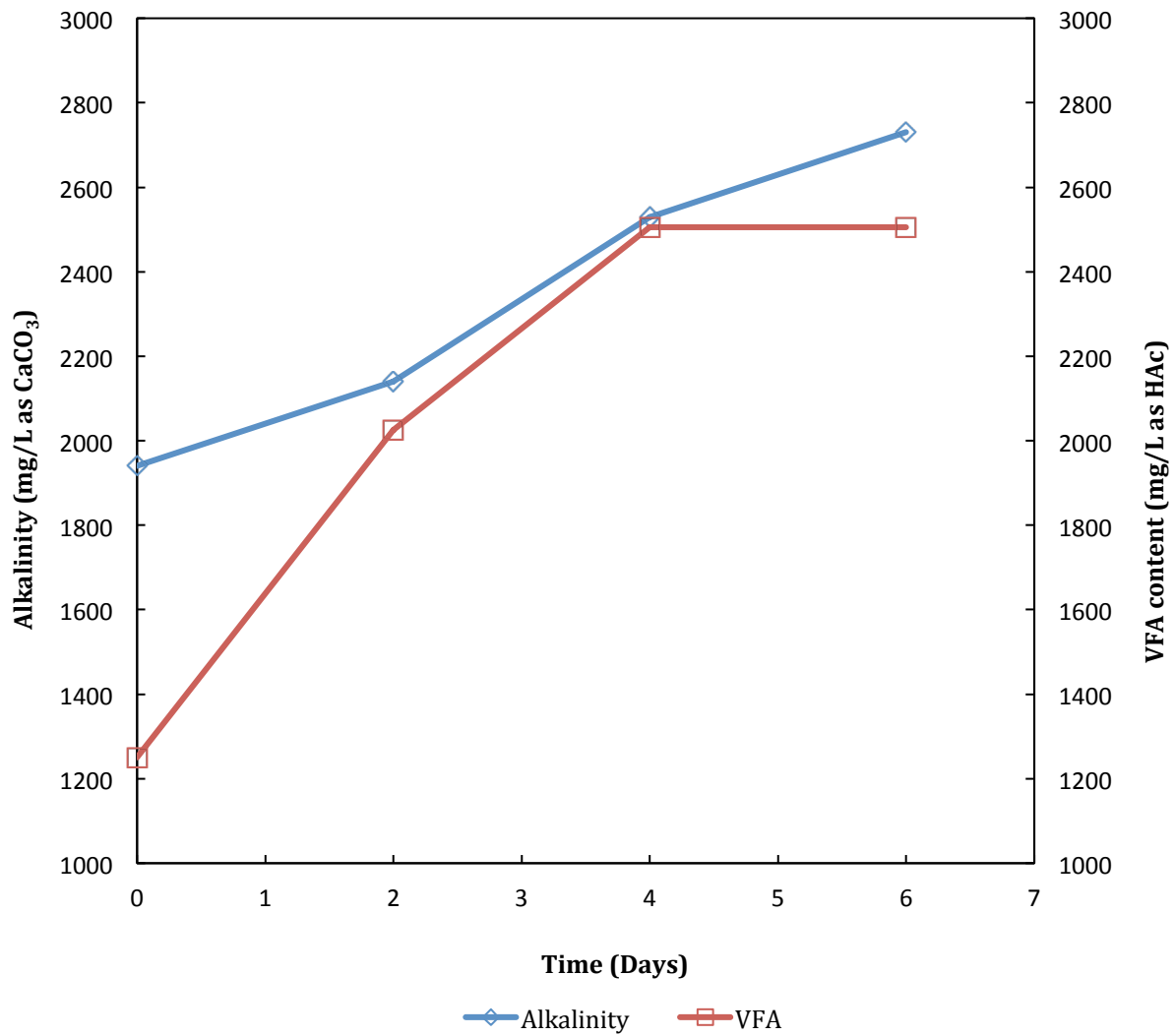


**Figure 4.13 pH and temperature results from semi-continuous system**

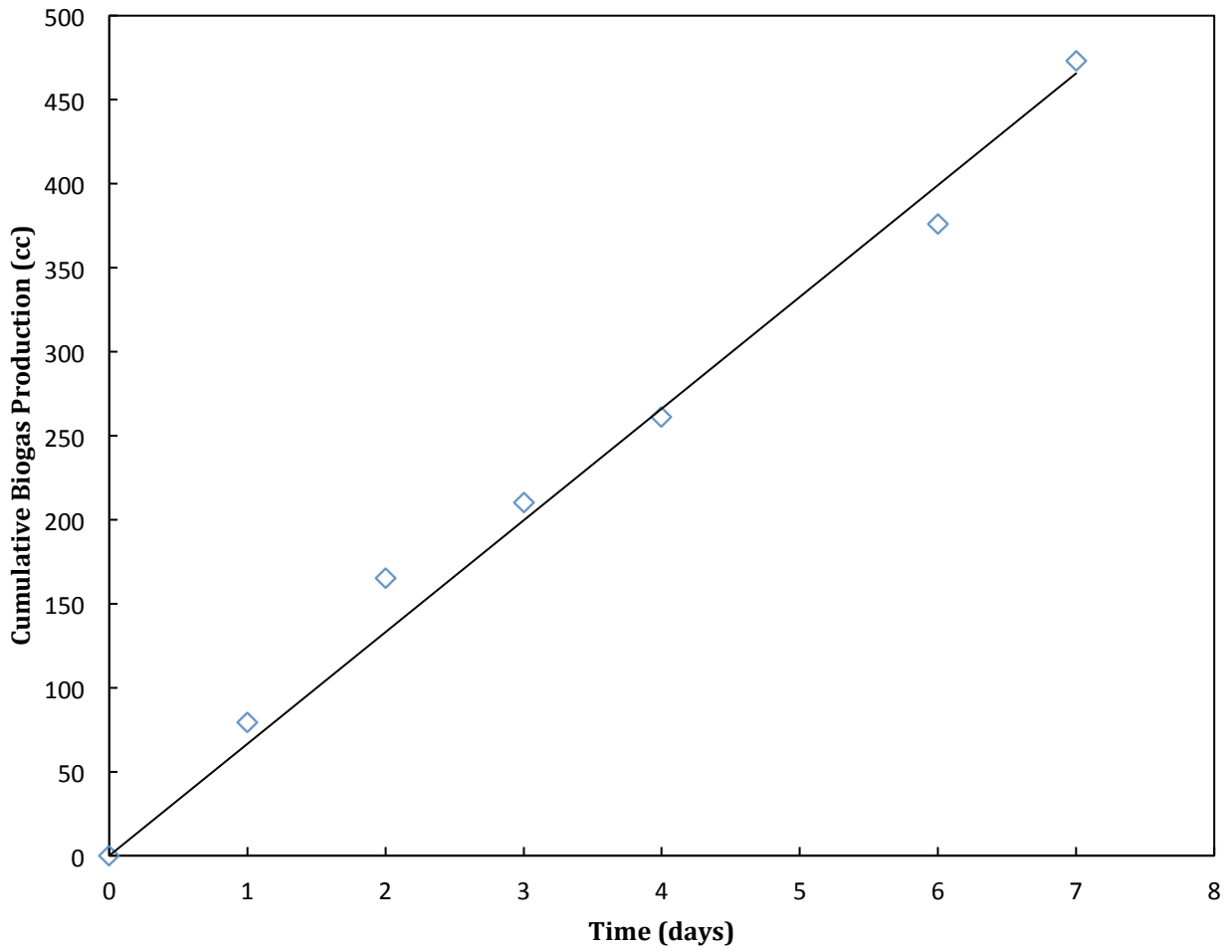
Alkalinity and VFA content were measured every other day during the testing period to limit reduction in the digesting volume (approximately 600 mL). This was a limitation of the semi-continuous apparatus, as more frequent testing would give better insight into the actions of the system. With a much larger reaction vessel, these two parameters could have been tested more often, while not greatly affecting the total volume of the digester. As seen in Figure 4.14, both the alkalinity and VFA content continued to rise after the initial dose of sodium propionate. There was expected to be an initial rise in both parameters as was seen with the addition of sodium propionate during parametric studies. However, in typical continuous systems, the alkalinity remains high and the VFA content remains at a minimum. By dosing the semi-continuous system with sodium propionate at the beginning of testing, digestion could have become slow due to a high acid content disrupting the system. This is shown in Figure 4.14 as the VFAs continue to rise until reaching a peak on day 4. The shock to the digestion system seems to be overcome towards the end of testing, as the alkalinity continued to rise while the VFA content remained constant. Extending the testing period may have allowed the system to balance itself. A longer test would have allowed the system to react to the chemical adjustment, possibly showing an increase in biogas production similar to that seen in parametric studies.

#### **4.5.2 Gas Production**

The data in Figure 4.15 show that gas production remained relatively stable throughout the week of testing. Slight variations in slope show an increase or decrease in production, but overall, gas production remained stable. It was expected that the system would, at minimum, maintain the same production rate throughout the experimental



**Figure 4.14 Alkalinity and VFA content measured during semi-continuous testing**



**Figure 4.15 Cumulative biogas production throughout semi-continuous experiment**

period, demonstrated as a straight line with a constant slope. Parametric studies indicated that the production would rise after adjustment with sodium propionate. Therefore, it was expected that the results would show an increase in slope after adjustment with sodium propionate at longer times.

Control samples for this experiment were run in parallel following the methods for parametric studies. These two control samples were not meant to be used for gas production comparison, but rather for comparison with previously obtained sludge samples to ensure that the sludge being used in the semi-continuous system compared well. The two samples, one with and one without adjustment with 10 M sodium propionate, were allowed to digest for a one week period in a controlled temperature bath (35 °C). The amount of sodium propionate in the adjusted control sample corresponded with the amount added to the semi-continuous system at the beginning of testing. Both samples produced slightly lower amounts of biogas when compared to previous samples in parametric tests, but gas quality did not noticeably drop. Production values can be found in Table 4.5. It was concluded that the semi-continuous system would maintain a high biogas quality and show an increase in production rate following adjustments determined during parametric studies.

The quality of the biogas was not measured throughout the semi-continuous testing period, but was determined on the final day of testing to be 38% CH<sub>4</sub>. This indicated that the increased acid content in the digester, as seen in Table 4.4, caused the methanogen activity to decrease. The alkalinity of the system remained at a high level due to the use of sodium propionate for adjustment. The acid build-up within the system caused product

**Table 4.5 Comparison of control samples used during semi-continuous testing and parametric samples**

<b>Parameter</b>	<b>Control Vial Samples (semi-continuous)</b>		<b>Parametric study-VFA content (Figure 4.8-day 7)</b>	
	<b>Control</b>	<b>Adjusted</b>	<b>Control</b>	<b>Sample 1</b>
<b>Quantity</b>	1.35 mmol	1.62 mmol	1.33 mmol	2.01 mmol
<b>Quality</b>	79.03% CH <sub>4</sub>	80.91% CH <sub>4</sub>	83.69% CH <sub>4</sub>	81.17% CH <sub>4</sub>

inhibition, further slowing the digestion process, affecting the quality of the produced gas and most likely affecting the quantity of produced gas. If the testing period were extended, it is possible that the digestion system would have overcome the acid build-up. If so, gas production might have showed an increase in daily production and gas quality would have improved.

## **CHAPTER FIVE CONCLUSIONS**

Optimization of the anaerobic digestion process resulted in the enhancement of biogas quantity and quality. Some adjustments proved to be vital while others proved to be ineffective. Batch testing upon the digestion process showed that pH was an effective indicator as to the stage of digestion. Through constant pH monitoring, each stage of digestion could be identified, providing a way for treatment plants to monitor digester activity.

It was determined through parametric studies that all tested parameters were coupled. Therefore, one parameter cannot be altered without affecting others. Biogas production was highest near a neutral pH. The optimum range was defined to be 7.0-7.5, as the samples within this range showed the highest mole fraction of methane throughout the testing period.

The optimum temperature for digestion fell within the mesophilic range (30-40°C). Operation within this range provided stable production for both parametric and semi-continuous testing. Highest production was achieved at 40°C, but energy balances showed that maintaining digestion within the lower portion of the mesophilic range would be more energy efficient.

Parametric testing upon alkalinity showed that a final tested range from 2,000-2,500 mg/L as CaCO<sub>3</sub> provided optimal gas production. The control sample, with no

chemical adjustment, showed the highest production of any sample tested. Alkalinity adjustment with magnesium hydroxide caused both the alkalinity and pH to rise. This was due to the dissociation of magnesium hydroxide, which increased the hydroxide content of the digest, increasing the pH.

Parametric adjustment of VFA content with sodium propionate altered both VFA content and alkalinity. This was caused as dissociation of sodium propionate creates a sink for  $H^+$ , allowing the alkalinity to increase. Biogas production varied depending upon the amount of VFAs added at the beginning of testing. High initial levels of added VFA caused the digestion system to struggle in recovering, while small adjustments made with added VFA showed increased production at longer testing times. It was also observed that dilution of the sludge mixture, resulting in lower solids and lower microorganisms in solution, caused lower production of biogas.

Pressure within the digestion system had a profound effect on the quality and quantity of produced biogas. Increased system pressure resulted in increased yield, methane content, and heating value of the biogas. This was due to the effect of pressure on the VLE of carbon dioxide. By increasing the carbon dioxide content in solution, gas production can be increased through enhanced reduction of carbon dioxide.

Semi-continuous testing showed consistent biogas production throughout testing. A rise was expected at longer testing times based on parametric studies. Temperature and pH remained within the determined optimum range, while the alkalinity and VFA content rose farther than expected. Biogas quality measured at the end of testing showed only 38%

methane within the sample. Therefore, it was concluded that a high acid content within the digest caused methanogen activity to decline, resulting in a lower quality and quantity of biogas.

## **CHAPTER SIX FUTURE SCOPE**

Optimization of the anaerobic digestion process proved to be very promising through experimental research, but there is still much work to be done within this field. Future research will focus on the effect of pressure upon the anaerobic digestion of sewage sludge. Pressure seems to be a deciding factor as to the quality and quantity of the produced biogas. Focus will be placed on developing a better understanding of the mechanism with which pressure effects digestion, as well as optimization of pressure within the anaerobic system. Developing an apparatus that allows for pressure control and monitoring within a continuous system will be important. Pressure also shows potential for use with gas cleaning. Development of a pilot-scale continuous system to control pressure within the digestion system is of great interest to test the cleaning ability.

The semi-continuous experiment was hampered by the length of testing. While pH and temperature were maintained within the determined optimum range, better optimization of the VFA content and alkalinity may lead to higher biogas production. Further parametric studies conducted within the semi-continuous system will be beneficial to the study of optimization. Optimal loading rates for volatile solids and optimized retention times within the anaerobic system would be beneficial to the production of biogas.

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## APPENDIX A EPA Methods

### Determining the Alkalinity of a solution (>20 mg/L as CaCO<sub>3</sub>)

1. Centrifuge 80 mL of partially digested WAS for 20 minutes at 2,500 rpm
2. Place 25 mL of supernatant in a flask
3. Check and record pH
4. Using 0.1N H<sub>2</sub>SO<sub>4</sub>, titrate sample to a pH of 4, recording amount used

#### Calculations

$$(\text{mL of H}_2\text{SO}_4 \text{ used})(100) = \text{mg/L as CaCO}_3$$

$$\text{Ex. (17.2 mL H}_2\text{SO}_4) (100) = 1,720 \text{ mg/L}$$

### Determining the Volatile Fatty Acid content of a solution

1. Continue titration of alkalinity sample to pH 3.5 using 0.1 N H<sub>2</sub>SO<sub>4</sub>
2. Place titrated sample on hot plate (heat for approximately 10 minutes) and allow to boil for 3 minutes (use stir bar to assist in boiling)
3. Allow to cool to room temperature by running under cold water for 5 minutes
4. Using 0.05N NaOH, titrate to pH 4.0, recording amount used (A)
5. Titrate to pH 7.0, recording amount used (B)

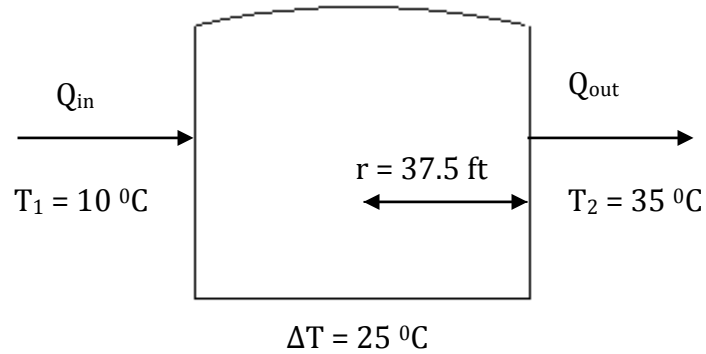
#### Calculations

$$(B - A) (50) = \text{volatile acids (mg/L as HAc)}$$

Example:

$$(5.3 - 0.7)(50) = 230 \text{ mg/L volatile acid}$$

**APPENDIX B**  
**Digester Calculations and Energy Balance**



$$V = \pi r^2 h$$

For 1 ft. of sludge per day,

$$V = 4,418 \text{ ft}^3 / \text{day}$$

$$4,418 \text{ ft}^3 \left| \frac{7.48 \text{ gal}}{\text{ft}^3} \right| \left| \frac{8.37 \text{ lb}}{\text{gal}} \right| = 276,600 \frac{\text{lb sludge}}{\text{day}}$$

$$Q = \dot{m} C_p \Delta T$$

$$\dot{m} = 276,600 \frac{\text{lb sludge}}{\text{day}} \quad C_p = 1,897.72 \frac{\text{J}}{\text{lb} \cdot \text{C}} \quad \Delta T = 25^\circ\text{C}$$

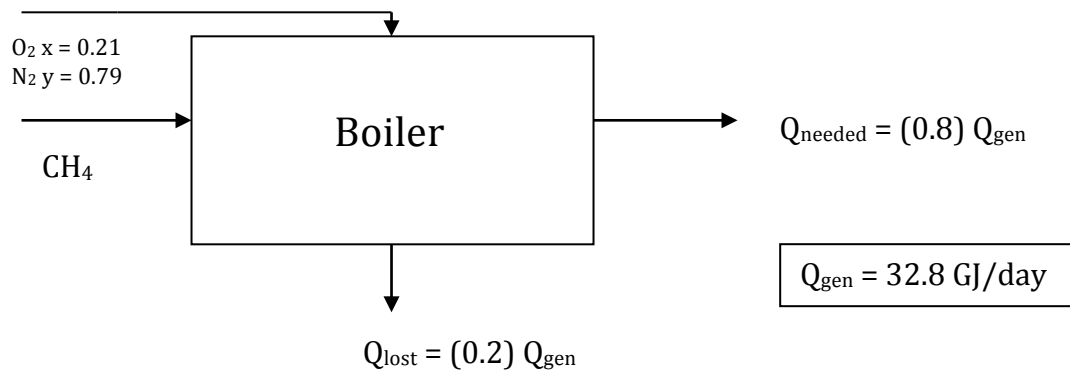
$$Q_{\text{needed}} = 1.31 \times 10^{10} \frac{\text{J}}{\text{digester day}}$$

$$Q_{\text{needed}} = 13.12 \frac{\text{GJ}}{\text{digester day}}$$

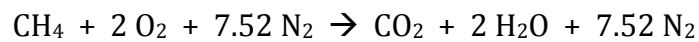
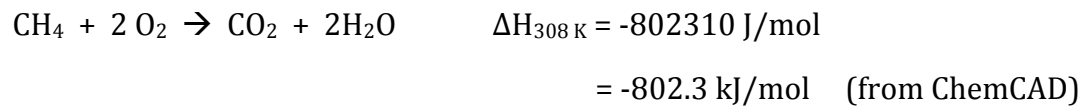
$$\text{For 2 digesters} \rightarrow Q_{\text{needed}} = 26.24 \frac{\text{GJ}}{\text{day}}$$

## Boiler

Assuming 80% efficiency



$$\Delta H = \Delta H_{308\text{ K}} + \Delta H_P$$



$$\Delta H_P = \langle C_P \rangle_H (T - 308 \text{ K})$$

$$\langle C_P \rangle_H = \sum n_i \langle C_{Pi} \rangle_H = R \left[ \sum n_i A_i + \frac{\sum n_i B_i}{2} T_o (\tau + 1) + \frac{\sum n_i D_i}{\tau T_o^2} \right]$$

$$T_o = 308 \text{ K} \quad (\text{exit temperature of biogas})$$

$$T = 366 \text{ K} \quad (\text{temperature exiting boiler})$$

	A	B (x10 <sup>3</sup> )	C	D (x10 <sup>5</sup> )
CO <sub>2</sub>	5.457	1.045	--	-1.157
H <sub>2</sub> O	3.470	1.450	--	0.121
N <sub>2</sub>	3.280	0.598	--	0.040

$$\sum n_i A_i = (5.457) + 2(3.470) + 7.52(3.280) = 37.0626$$

$$\sum n_i B_i = 8.404 \times 10^{-3}$$

$$\sum n_i D_i = -6.142 \times 10^{-6}$$

$$\tau = \frac{T}{T_o} = 1.19$$

$$\begin{aligned} \langle C_p \rangle_H &= (8.314) \left[ 37.0626 + \frac{8.404 \times 10^{-3}}{2} (308.15)(\tau + 1) + \frac{-6.142 \times 10^{-6}}{\tau(308.15)^2} \right] \\ &= (8.314) [37.0626 + 2.835 - 5.435 \times 10^{-11}] = 331.71 \frac{J}{mol} \end{aligned}$$

$$\Delta H = \Delta H_{308K} + \Delta H_P$$

$$= -802.3 \frac{kJ}{mol} + 0.3317 \frac{kJ}{mol}$$

$$\Delta H = -801.97 \frac{kJ}{mol}$$

$$Q_{gen} = 32.8 \text{ GJ}$$

$$32.8 \text{ GJ} \left| \frac{10^9 J}{1 \text{ GJ}} \right| \left| \frac{1 \text{ mol } CH_4}{801970 J} \right| = 40,900 \text{ mols } CH_4$$

$$\text{Based on } \rho(35^\circ\text{C}) = 0.64 \frac{kg}{m^3}$$

$$40,900 \text{ mols } CH_4 \left| \frac{16 \text{ g}}{mol} \right| \left| \frac{kg}{1000g} \right| \left| \frac{m^3}{0.64 \text{ kg}} \right| = 1022.5 \frac{m^3}{day} CH_4$$