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Anaerobic Digestion Process Stability and the Extension of the ADM1 for Municipal Sludge Co-Digested with Bakery Waste

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ANAEROBIC DIGESTION PROCESS STABILITY AND THE EXTENSION OF THE ADM1 FOR MUNICIPAL SLUDGE CO-DIGESTED WITH BAKERY WASTE

by

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ABSTRACT

Anaerobic Digestion Process Stability and the Extension of the ADM1 for Municipal Sludge Co-Digested with Bakery Waste

by

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Utah State University, 2016

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Uncertainty about anaerobic digestion process stability is the main issue preventing more widespread use of the process as a source of energy recovery in wastewater treatment facilities. The overall objective of this research was to study the feasibility of enhancing biogas production inside wastewater facilities using co-digestion of municipal sludge with bakery waste. Another objective was to improve the stability index and a mathematical model that can be useful tools to predict the process stability of municipal sludge digestion alone, and when it is mixed with bakery waste, as a substrate for microorganisms.

Experiments were conducted in three phases. In phase 1, a full-scale anaerobic digester at Central Weber Sewer Improvement District, Ogden, UT, receiving a mixture of primary and secondary sludge, was monitored for one hundred days. Chemical oxygen demand (COD), and volatile solids (VS) mass balances were conducted to evaluate the stability of the digester and its capability of producing methane gas. The COD mass balance accounted for nearly 90% of the

methane gas produced while the VS mass balance showed that 91% of the organic matter removed resulted in biogas formation. Other parameters monitored included: pH, alkalinity, VFA, and propionic acid. The values of these parameters showed that the digester was running under stable steady state conditions. At mesophilic temperature, the stability index was determined and equal to $\frac{0.40\ L\ (CH_4)}{g\ (\Delta VS)}$

In phase 2, the feasibility of adding BW to MS was tested in batch reactors scale. The biogas production was enhanced and the digester was stable until the range of 37-40% of BW to 63-60% of MS. The ADM1 coefficients were modified to accurately predict the digester performance. The modified model outputs (pH, VFA, and methane) were within acceptable ranges when compared with the observed data from the batch reactors.

In phase 3, the feasibility of MS and BW were tested using an Induced Bed Reactor (IBR) with a 50:50% ratio of MS:BW (COD basis). The process was stable during different hydraulic retention times and the ADM1 was modified to predict the stability of the process in the IBR.

(144 pages)

PUBLIC ABSTRACT

Anaerobic Digestion Process Stability and the Extension of the ADM1 for Municipal Sludge Co-Digested with Bakery Waste

Morris E. Demitry

The anaerobic digestion process is used to treat and convert waste organic matter to biogas (principally methane and carbon dioxide) through biological, chemical and physical reactions. The biogas can be used as a source of energy recovery. In order to increase the biogas production rate, two different kinds of waste (municipal wastewater treatment sludge and bakery waste) were mixed together to enhance the anaerobic process and increase the biogas production in pilot scale reactors. The process succeeded in increasing biogas production and at the same time kept the process of treatment effective when high rates of organics were fed to the reactor.

This process can provide communities with both economic and environmental benefits. The anaerobic process converted the large quantity of waste to biogas that can be used as a fuel for heating.

In this research an existing mathematical model was modified in order to easily predict the performance of the process. This modified model can be used to determine the benefits of the process and to predict the point of failure of the treatment process as increasing amounts of the wastes reach concentrations that cannot be handled by the anaerobic microorganisms. The model is a useful tool to reduce the uncertainty regarding the operation of the process.

DEDICATION

I dedicate my dissertation to the soul of my father, Elya Demitry, and my mother Siley Ishak, for their effort and support in helping me reach my higher education. I also want to dedicate this to my wife Mariana Demitry, for her support to me. I also dedicate it to my children who motivated me to reach this point. Moreover, I dedicate my thesis to all my brothers in Egypt, Sudan and Canada (Magdi Demitry, Makram Demitry, Michael Demitry, Magdolin Demitry, Makariuos Demitry and Merviet Demitry) for their efforts with me.

Thanks to all of you

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Thanks are extended to the soul of my father, Elya Demitry and my mother Siley Ishak for their love and support. Thanks you Marianna and my children, Mina, Matthew and Madonna for being my strength from beginning to end.

Finally, I would like to thank my Lord, Jesus Christ, for helping me find peace and broaden my mind.

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CHAPTER 1

1. Introduction

Producing renewable energy is an important challenge for the world today because it is often costlier than the harvesting of fossil fuels. Finding new and economically sustainable sources of energy to fulfill the world energy demand is a technological and economic challenge. Use of the anaerobic digestion of sludge may represent a cost-effective approach to generate a sustainable and renewable energy source. It was reported by the U.S. Energy Information Administration (EIA) that in 2012 about 82% of the primary energy consumption was from fossil fuels, which consisted of 36% petroleum, 20% coal and 26% natural gas, while renewable energy consumption was only 9% (U.S.E.I.S. 2015) . The increasing price of fossil fuels and the change in the climate encourages researchers to find an alternative source of renewable energy. Methane gas, produced naturally from wastewater treatment facilities as a final product of the biodegradation of municipal sludge, is considered an alternative renewable energy source. Methane is a very powerful gas; the heating value of methane is 23,800 British thermal units per pound (BTU/Ib). One pound of methane has 25 times more heat value in the atmosphere than a pound of carbon dioxide. Methane can be captured from the anaerobic digesters as a final product from the anaerobic digestion process of organic matter.

Anaerobic digestion of organic matter consists of three major steps, namely hydrolysis, acidogenesis and methanogenesis. These three steps involve the metabolism of hydrolytic bacteria and other microorganisms, acidogenic bacteria and methanogenic archaea, respectively. This process involves the degradation of organic materials under anaerobic conditions by microbial organisms and leads to the formation of biogas (a mixture of methane gas and carbon dioxide), a good source of renewable energy (Metcalf et al. 2013). Anaerobic digestion offers numerous significant advantages, such as low residual sludge production, low energy requirement and possible energy recovery. Because of its advantages, it has been used widely in the treatment of wastewater but use has been limited in the treatment of organic industrial waste(Parkin and Miller 1983).

Utilizing an anaerobic treatment process is being considered by waste treatment entities, including wastewater treatment plants, as one possible means of recovering energy in the form of methane gas while at the same time reducing the pollutant load of the organic matter. The resulting methane production from the anaerobic digestion of municipal sludge could yield an important fraction of the current natural gas consumption in the US(Metcalf et al. 2013). Despite the wide usage of the process for decades, anaerobic digestion is still one of the least understood processes in waste treatment; the process is complicated, difficult to study because it depends on the chemical and biological activities inside the anaerobic digester ecosystem (Kroeker et al. 1979).

Table 1. Heating value for different kinds of fuel (TET 2015)

Fuel	Phase	Heating Value (Btu/Ib)
Methane	Gas	23,811
Natural Gas	Gas	19,500
Hydrogen	Gas	61,084
Acetylene	Gas	21,569
Propene	Gas	20,990

The overall objectives of this research are to develop monitoring concepts and a predictive tool useful in controlling the co-digestion process stability also, determine the stability of the anaerobic digestion process when injecting bakery waste with municipal sludge under different ratios and hydraulic retention times.

2. General Background

Many advantages of using anaerobic digestion to treat the sludge in municipal wastewater have been reported. Anaerobic treatment will reduce the volume of sludge effectively (1,000 kg of sludge can be reduced to 50 kg), besides, producing biogas which is a source of renewable energy, a high rate of pathogens destructions can be achieved, and digested sludge is generally free of objectionable odors (Turovskiĭ and Mathai 2006).

An important disadvantage of the anaerobic process is its propensity to be upset due to toxic substances (Ye Chen 2007) or the accumulation of organic acids. It may require increasing alkalinity by soda ash addition to keep the process working well. The cost associated with these additions can be substantial. These factors have direct effects on process stability. Stability has been defined as the harmonic relations between acid formers and methane formers (Bitton 2011). In anaerobic digestion, the acid forming and the methane forming microorganisms differ widely in terms of physiology and nutritional needs (Burton 2004). Environmental factors known to be important in affecting anaerobic digester stability include ammonia concentration, pH, concentrations of various cations, sulfide concentration, volatile fatty acid concentration, partial pressure of hydrogen, and the carbon to nitrogen ration (C:N) of the feed stocks.

[1.21] Ammonia:

Ammonia is produced by the biological degradation of organic matter that includes proteins and urea. Ammonia (NH3(g)) causes inhibition through a change in the intercellular pH and can limit the rate specific enzymes reactions (Wittmann 1995). In order to avoid toxicity from ammonia, the concentration should never reach the range between 1500-3000 mg/L (Bitton 2005).

[1.22] Carbon, nitrogen and phosphorus ratio:

The presence of C: N: P is important to maintain optimum performance of the digestion. For optimum digestion, C: N:P is supposed to be 700:5:1 (Lettinga 1995), while another study reported that, the optimum ratio for C:N is 25-30:1(Polprasert 1989). The process of co-digestion of different substrates may change the ratio of the C: N: P and may inhibit the bacterial activities.

[1.23] pH

pH affects the growth of microorganisms (Bitton 2011). Moreover, pH affects the distribution of total ammonia nitrogen (TAN) between toxic NH3(g) and innocuous NH_4^+. Optimum performance of the anaerobic microorganisms will be reached with neutral pH (6.8-7.2) (McCarty 1973). Failing to maintain pH within an appropriate range could cause reactor failure (Kroeker 1979). Optimum performance of the anaerobic microorganisms will be reached with neutral pH (6.8-7.2) (McCarty 1973). Failing to maintain pH within an appropriate range could cause reactor failure (Kroeker 1979).

[1.24] Concentration of ions:

Certain ions such as K^+, Fe^{+3} Mg^{+2}, and Ca^{+2}, are inhibitory to methanogenesis, K^+ concentration above 3 mg/L are toxic to microorganisms (Chen et al. 2008). Fe^{+3}, was reported to halt 52-82% methanogenesis activities with concentration of 21 mg/L or above because Fe^{+3} could deactivate enzymes of microorganisms by reacting with their functional groups (Zhang et al. 2009). Mg^{+2} was reported to be inhibitory to methanogenesis when it reaches 720 mg/L, while Ca^{+2} was moderately inhibitory to microorganisms in concentrations above 300 mg/L (Schmidt and Ahring 1993; Yu et al. 2001).

[1.25] Sulfide:

Sulfide is a common constituent of many industrial wastewaters and in an anaerobic digester, sulfate is reduced to sulfide by sulfate reducing bacteria (Iman W. Koster 1987) . Two kinds of inhibition are caused by sulfide: first, toxicity from the competition for a common organic matter substrate and that cause stress for methanogenesis and second, the toxicity of sulfide to various bacteria groups (Bitton 2011).

[1.26] Volatile Fatty Acids (VFA)

VFA including acetic, butyric, valeric and propionic acid are reported to be inhibitory to methanogenesis when reaching above 2000 mg/L(Siegert and Banks 2005). Propionic acid alone is toxic to both acid-forming bacteria and methanogenesis in concentrations above 900 mg/L (Wang et al. 2009). Methane production is decreased by 50% when VFA concentration is >2200 mg/L at mesophilic conditions (Gallert and

Winter 1997). At any rate, a direct relation between accumulation of VFA and a drop in pH value was reported (Metcalf et al. 2013).

[1.27] Hydrogen gas partial pressure:

A negative impact of the increase of hydrogen gas partial pressure on acidogeneses bacteria has been reported. The partial pressure of the hydrogen gas should be less than 10^{-4} atm in order to avoid stress in the acidogenic bacteria (Burton 2004; Woods et al. 1980).

[1.28] Enhancing biogas production from wastewater treatment facilities

Enhancing biogas from the anaerobic digestion process and keeping the process stable at the same time is a challenge. Recently, researchers have focused on co-digestion of food wastes or fats, oil and grease (FOG) (Fang et al. 2011; Iman W. Koster 1987; Jeong et al. 2005; Kabouris et al. 2009; Parkin 1983 ; Wang 2006). The benefit from co-digestion compared to traditional anaerobic digestion was substantial. There was an increase in methane by 46% when municipal wastes were co-digested with FOG with 15% volatile solids (VS), and no inhibition was observed (L. Martín-Gonzáleza 2010). The process of co-digestion increased the destruction of VS increasing the quantity of biogas and methane (Kabouris 2008).

The chemical composition of substrate co-digested with municipal sludge plays a major role in the process stability and in the enhancement of biogas production. Careful study is still required to evaluate different kinds of industrial waste that can be digested with municipal sludge. One of these industrial wastes is bakery waste. Bakery waste contains carbohydrates including starch and sugars, fats, and proteins that are anticipated to be readily degraded by digester hydrolytic microorganisms and, in turn, enhance biogas production.

The bakery industry is one of the main food industries all over the world, bakery products are categorized as bread, bread roll and pastry products that include, donuts, cakes, biscuits and pies. There are almost 7,000 bakery operations in the USA. The bakery industry is a dynamic part of the USA economy and accounts for $311 billion in total economic outputs or approximately 2.1% of the Gross Domestic Products (GDP) in USA (Association 2004) . Bakery wastewaters are rich in carbohydrates and lipids (70% carbohydrates, 20% lipids and lack of proteins) and have high COD values 93 g/L. The bakery industry in the USA discharges more than 300,000 gal/day as wastewater (Lawrence K. Wang 2006). Since the population of the USA was increased, accordingly an increase in the population and the bakery processors is expected to be increased in 2016 and bakery waste discharge is expected to be increased also in 2016. However, the volume of 300,000 gal/day is easily can be treated by injecting it to the digesters at the wastewater treatment facilities instead of constructing pretreatment unit, especially to treat the BW. However, in order to treat the bakery waste aerobically inside the bakery processors may cost the processors an amount of $ 10,000,000 to construct the required pretreatment unit ((Arsova 2010). Moreover, the operation cost of the aerobic treatment is $ 110 per ton of waste. This research may find an alternative for treating the BW anaerobically using an existing municipal anaerobic digesters instead of aerobic treatment. Bakery waste and municipal sludge characteristics are shown in Table 2.

Table 2. Municipal sludge bakery waste characteristics; data were collected from CWSID and CSM Bakery Products, Ogden, UT

Parameters	Unit	[1]Municipal Sludge	[2]Bakery Waste (Pan Wash)	[3]Bakery Waste (Machine Wash)
pH		7.15±0.09	5.66 ± 0.25	4.4 ± 0.54
[3]TS	%	5.15 ± 0.34	6.69 ± 0.22	9.35± 1.22
[3]VS	% of TS	84 ± 2.34	91 ± 0.65	96 ± 1
[3]COD	g/L	74.49 ± 2.52	93.67 ± 2.11	175± 1.37
Alkalinity ($CaCO_3$)	mg/L	4113±229	[3]BDL	BDL
[3]TKN	mg/L	1918± 80	BDL	BDL
NH_3-N	mg/L	1123±12	BDL	BDL

1.Municipal sludge samples were collected in the period of August, 2013 - February 2016

2.Bakery Waste samples were collected in the period of August, 2014 - February 2016

3.Total solids, Volatile Solids, Chemical Oxygen Demand, Total Kjeldahl Nitrogen, Below Detection Limit.

Based on the anaerobic digestion processes' characteristic of being upset easily, it is important to use a predictive tool to make accurate estimates of the performance of the digester in co-digesting these wastes.

Even though the BW contained high organic matter, it cannot be treated with anaerobic digestion without dilution or addition of a co-substrate because of its characteristics (pH, VFA, TKN, NH3). The BW could be digested with other kinds of municipal or industrial waste to reach a stable digestion process. Bakery waste (BW) may be shown to be a promising substrate if co-digested with municipal sludge and the outcome of this process should be simulated as accurately as possible using computer modeling in-order to study the stability of the process

[1.29] The anaerobic digestion model number 1 [ADM1]

The Anaerobic Digestion Model 1 (ADM1) model was established by the IWA task group for mathematical modeling of anaerobic digestion process (Batstone and Keller 2003). The ADM1 is a mathematical model that has open structure, common nomenclature integrating biokinetics with association-dissociation; gas–liquid transfer; the internal overall bacterial reactions in terms of hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The model uses constants and coefficients to describe the physical-chemical and biological reactions (Figure 1).

in the ADM1 model, the organic matter is determined based on the chemical oxygen demand (COD). The model uses some variables to explain the behavior of soluble and particulate components. The influent COD is classified to biodegradable and non-biodegradable. Usually it is difficult to determine the percentage of these parameters since most of the time sludge COD is not determined (Parker 2005). Moreover, there are no enough information about how the fraction of carbohydrates, proteins and lipids can be estimated for municipal sludge (Shang et al. 2005).

The formation of methane, which is the ultimate product, occurs from the use of two major substrates, acetic acid and hydrogen, as shown in the following equations (Burton 2004).

$$CH_3COOH \rightarrow CH_4 + CO_2 \tag{1}$$

$$4H_2 + CO_2 \rightarrow CH_4 + H_2O \tag{2}$$

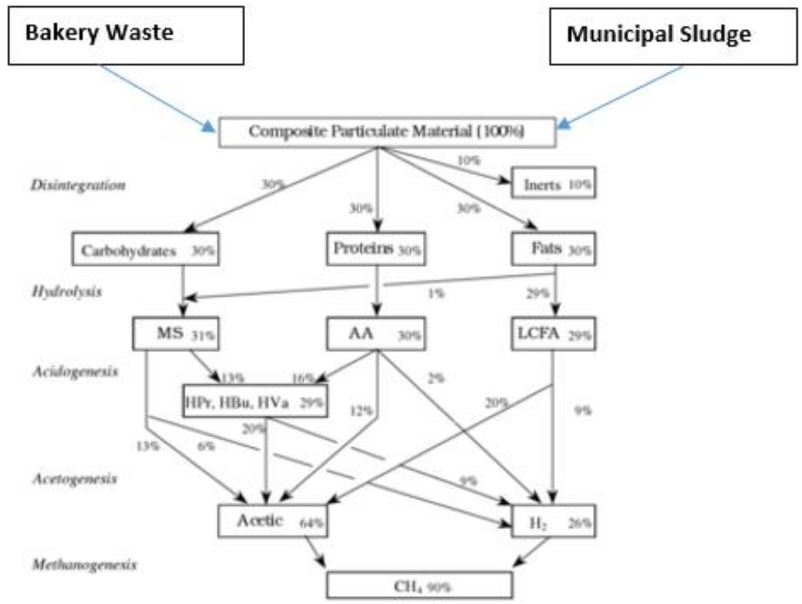

Figure 1.The COD Flow Chart of the ADM1 adapted from ((Batstone et al. 2002)

Two thirds of methane was produced from aceticlastic methanogenesis while one-third from hydrogenotrophic methanogenesis in a study reported by (Bitton 2005; Mackie and Bryant 1981; Metcalf et al. 2013) (Equation 1). However, other studies shows the opposite, that most of methane is produced through hydrogenotrophic methanogenesis (Equation 2)((Demirel 2014). In those studies, hydrogenotrophic methanogens were the majority of the methanogen's populations (Demirel and Scherer 2008).

3. Research Problem Statement

Determining anaerobic digester stability is important to keep the process functioning well. Many researchers ((Angelidaki and Ahring 1992; Angelidaki and Ahring 1993; Hill and Holmberg 1988; Kroeker et al. 1979; McCarty 1964; Siegert and Banks 2005) reported different ways of indicating stability, but there is no simple and direct definition of the term "stability"(Morris E. Demitry 2015). Monitoring the anaerobic digesters by collecting samples from the municipal sludge from influent and effluent sides to measure the stability indicators like pH, TVFA, propionic acid, ammonia nitrogen NH_3, methane gas (CH_4) will help to understand the term ‘stability.’ However, the steady state of the anaerobic digestion process is achieved when the digesters were operating at or near their recommended design levels (neutral pH, TVFA< 2000 mg/L, propionic acid < 900 mg/L, NH_3 < 1500 mg/L) and when gas production and gas rates were relatively constant (±10% per day) (Kroeker et al., 1979). Process stability is defined as the biochemical balance between acid formers and methane formers.

On the hand, the instability is usually indicated by the increase in the concentration of volatile acids, and a decrease in methane gas production (Chen et al. 2008). In anaerobic digestion, the acid forming and the methane forming microorganisms are different in terms of physiology, nutritional needs, growth kinetics, sensitivity to environment changes (Chen et al. 2008). The primary cause of reactor instability is the failure to maintain the balance between those two groups of microorganisms (Demirel 2002).

In fact, studies of the anaerobic digestion process are confusing since there are several situations that can play a significant role in the anaerobic process’s stability. For example, does the stability of the digestion process depend on the digester temperature, mesophilic or thermophilic, does stability depend on VFA concentrations or un-ionized VFA concentrations or alternatively, does it depend on ammonia toxicity and what are the toxic concentrations to the microorganisms? It is important to find a numeric value, a stability index that can reflect stable digester performance in an easy way and can be used as a quick tool for stability verification for full-scale digesters (Morris E. Demitry 2015).

Food wastes are the second largest component of Municipal Solid Waste (MSW) generation in the United States (EPA 2012). Food wastes may come from kitchen wastes, leftover food, plate waste and restaurants order returns and from industrial sources. The 14.5 % of the food waste (Figure 2) may need some sorting before being sent to the municipal facilities, which may add some cost to the overall process. Examples of industrial food wastes are bakery waste and cheese whey. However, less than 3% of food waste is recovered or recycled (EPA 2012).The amount of food waste is expected to be increased in 2016 since the population of USA was increased by 10% since 2012.

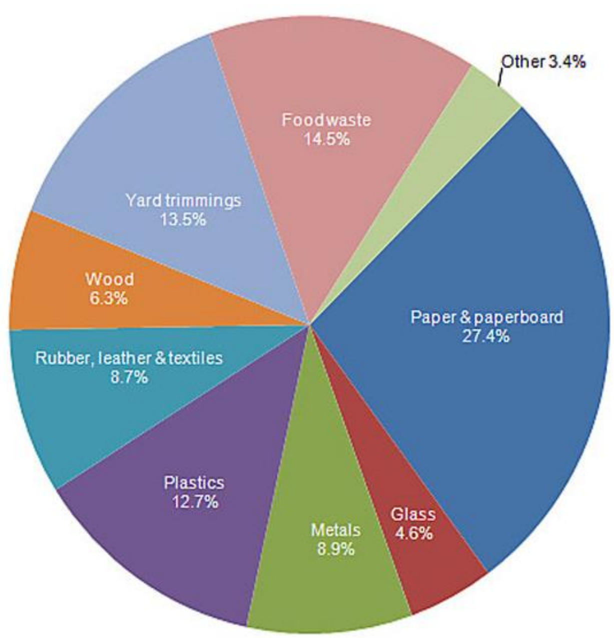

Figure 2.Total Municipal Solid Waste (MSW) (EPA 2012)

Landfill disposal of food wastes not only wastes money and energy invested during food production, it can also cause serious environmental problems. Food wastes, consist almost entirely of organic materials like carbohydrates, proteins and lipids, they easily and quickly digest in landfills, where large amounts of methane and CO_2 gas are produced which affect the atmosphere. According to the EPA, more than 20 percent of all human-related methane emissions are from landfill gas. Methane has an impact of global warming potential 21 times higher than carbon dioxide (EPA 2012).

The advantages of using anaerobic digestion process and the co-digestion of different kinds of organic matter especially food wastes have been described. Still the lack of certainty in applying the process of co-digestion at full scale, especially in a municipal sludge wastewater treatment plant, needs more investigation. The uncertainty of having the digestion process fail prevents treatment plant operators from running the full-scale process and evaluating it, since the cost of failure is substantial in terms of regulatory compliance, environmental degradation, and economic impact.

In the USA, some wastewater treatment plants considered the process of co-digestion for a short period. The King County, Washington treatment plant started the process of food-waste co-digestion with municipal sludge in 2011. The process was stopped after 1 month due to the increase of the percentage of CO_2 that affected the pH values besides the accumulation of inhibitory compounds inside the system when the FOG: sludge ratio, based on volatile solids (VS), reached 20:80 (KCWTD 2015). The second plant to try food waste co-digestion was Central Valley Wastewater Treatment Plant, Utah. They tested food waste from restaurants too. The process was stopped because of unstable gas production which could not be used in the co-generator system to produce power and alkali (soda ash) needed to be added to maintain an acceptable pH, which affected the budget of the project. Both wastewater treatment plants are investigating other alternatives for industrial wastes to be digested in the meantime.

Additional issues, beside stability, that should be considered in order to improve the anaerobic digestion process as an alternative renewable energy source are the costs of the transportation, grinding, mixing and pumping of the food waste to the digester. Food waste is associated with high saturated fats and unsaturated fats which lead to build up of long chain fatty acids which inhibit both acidogenic bacteria and methanogenic archaea ((Koster and Cramer 1987).

Further study is required in this field, to evaluate the increase in biogas and methane recovery inside the wastewater facilities and to measure the stability of the process and its limitations. Bakery waste is considered to be an attractive substrate for the microorganisms since it includes high organic matter (COD= 93 g/L) that is easily biodegradable but it is important to test and evaluate it. Moreover, bakery wastes include low proteins and lipids which may reduce the potential for inhibition and toxicity due to ammonia and long chain fatty acids. However, bakery waste may include toxic materials, like preservatives (sulfites, propionic acid, sodium nitrite, flavor agents, etc.).

The internal biochemical reactions between these materials and the other process reactions (TVFA, long chain fatty acids)(Chen et al. 2008), may inhibit the microorganisms which would be reflected in a negative impact on process stability.

From this point of view, it is important to develop an accurate mathematical model (ADM1), to simulate and predict the digester's performance stability due to the impact of injecting BW into a full-scale digester, thus reducing the potential for digester failure. A test application of the ADM1 could not predict accurately the new situation of mixing two different substrates together, but the model was generally accurate when applied for municipal sludge alone. A useful model would predict the situation with high ratios of BW mixed with sludge (10:90 %, 20:80 %, 30:70 %, 40:60 %, 50:50 % (BW: sludge, respectively)) that cannot be tested with full-scale digesters due to the high risk of failure. Moreover, evaluation and testing of the reactor with different retention times gives an idea about the digester performance and the ADM1 sensitivity in that case. The retention times are: 27, 20, 18, 12, 9 and 6 days respectively or until the failure point is detected.

4. Research Objectives

1. Develop a stability index that can reflect a full-scale reactor's steady state condition and can define the stability of the anaerobic digestion process in a numeric value.
2. Examine and evaluate the anaerobic digestion stability with BW mixed with MS (in different ratios) using fully mixed batch reactors, also develop an existing model (ADM1) to accurately predict the digester performance and the overall stability in this case. The BW used is this scenario is the waste collected from the pan wash (sugar water).

3. Examine and evaluate the process stability when BW is mixed with MS (50:50% COD basis) using the induced bed reactor (IBR) and also modify the ADM1 model to predict the overall stability process and the IBR performance. The BW used in this scenario is the waste collected from the machine wash.

CHAPTER 2

Defining Full-Scale Anaerobic Digestion Stability: The Case of Central Weber Sewer Improvement District

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Abstract

A full-scale anaerobic digester receiving a mixture of primary and secondary sludge was monitored for one hundred days. A chemical oxygen demand (COD), volatile solids (VS), and mass balance were conducted to evaluate the stability of the digester and its capability of producing methane gas. The COD mass balance could account for nearly 90% of the methane gas produced while the VS mass balance showed that 91% of the organic matter removed resulted in biogas formation. Other parameters monitored included: pH, alkalinity, VFA, and propionic acid. The values of these parameters showed that steady state had occurred. At mesophilic temperature and at steady state performance, the anaerobic digester stability was defined as a constant rate of methane produced per substrate of ΔVS (average rate=0.40 L/g). This constant rate can be used as stability index to determine the anaerobic digestion stability in an easy and inexpensive way.

Keywords: anaerobic digestion, mass balance, renewable energy, steady state, stability, stability index

1. Introduction

Producing renewable energy is a challenge for the world today because it is often costlier than the harvesting of fossil fuels. Finding new and economically sustainable sources of energy to fulfill the world energy demand is a technological and economic challenge. Use of the anaerobic digestion of sludge may represent a cost-effective approach to generate a sustainable and renewable energy source.

Anaerobic digestion produces biogas, which consists primarily of methane (50 to 75% on a volumetric basis) as well as carbon dioxide (25 to 50%). The methane produced from the anaerobic digestion of municipal sludge, animal and crop wastes can cover up to 20% of the natural gas consumption in the US (McCarthy, 1973). The average energy content of biogas is approximately 600 to 800 British Thermal Units (BTUs) per cubic foot (ft3), which compares favorably to the energy content of natural gas (approximately 1,000 BTUs per ft3).

A primary benefit of using anaerobic digestion for the generation of renewable energy is that it is a standard sludge treatment process utilized in many municipal wastewater treatment plants. In the anaerobic digestion process, specific groups of facultative and obligate anaerobic microorganisms act in concert to metabolize organic matter associated with sludge, resulting in the production of methane gas. The important groups of microorganisms found in anaerobic digesters include the hydrolytic, acidogenic bacteria and methanogenic archaea (McCarthy, 1964).

Hydrolytic bacteria convert the complex organic matter, like carbohydrates, fats, and proteins to simple compounds like sugar, fatty and amino acids; the acidogenic bacteria are responsible for converting these intermediate compounds to fermentation products including volatile fatty acids (VFA), hydrogen, and carbon dioxide. The methanogenic archaea utilized the fermentation products to produce methane. One group of methanogenic archaea, the aceticlastic methanogens, split acetate into methane and carbon dioxide, while the other group, called hydrogen-utilizing methanogens, uses hydrogen and carbon dioxide to produce methane(Turovskiy and Mathai 2006)

Defining stability is a challenge; many researchers reported different ways in order to indicate stability, but there is no simple and direct definition of the term “stability.” The best way to control the anaerobic digestion process is through studying the anaerobic digester steady state besides defining the term ‘stability.’ Steady state was assumed to be occurring when digesters were operating at or near their controlled and fixed-variable design levels and when gas production and gas rates were relatively constant(Kroeker et al. 1979). Process stability is dependent upon maintenance of the biochemical balance between acid formers and methane formers while instability is usually indicated by a rapid increase in the concentration of volatile acids with a concurrent decrease in methane gas production (Kroeker et al. 1979). Cohen et al. (1981) have discussed the influence of phase separation on the anaerobic digestion stability. Methane reactors with one-phase system and two-phase systems were subjected to gradually increasing feed rate of glucose until the maximum load was reached. The results pointed to the fact that the stability of the two-phase reactor was more than one phase since all the VFA broke down immediately unlike the one-phase reactor (Cohen et al., 1981).

At any rate, the previous studies for stability are confusing since there are several situations that can play a significant role in the anaerobic process's stability. For example, does the stability of the digestion process depend on the digester temperature, mesophilic or thermophilic? Does stability depend on VFA concentrations or un-ionized VFA concentrations or alternatively, does it depend on ammonia toxicity, and what are the toxic concentrations to the microorganisms such as nitrogen? Clearly, defining stability is a challenge, because there is no simple and direct definition of the term "stability."

Failure to establish a reproducible digester stability metric(s) could result in catastrophic failure of the anaerobic digestion process as well as impairment in the discharged water quality.

In this study, the performance of a full-scale anaerobic digester operating at mesophilic temperatures (i.e., 36 °C or 98 °F) has been monitored for over one hundred (100) days. Collection and analysis of operational data from the anaerobic digesters at Central Weber Sewer Improvement District, Ogden, Utah, served as the scientific basis for defining stability. The goal of the study was to establish and quantify the range of specific operational parameters that could define digester operational stability. Enhancing the production of biogas from the digestion of sludge and other organic matter requires the development of a simple and cost-effective performance tool that can gauge the stability of the digester environment.

2. Objectives

1. Collecting the digester's operational data including biogas production, percent methane in biogas, total solids, volatile solids destruction, influent and effluent chemical oxygen demand, digester pH, alkalinity, and volatile fatty acid concentrations in order to study steady digester operation.
2. Using statistical analysis for the operational parameter behavior to determine a universal performance metric (stability index) that reflects steady state for the digester operation.

Background about Central Weber Sewer Improvement District

Central Weber Sewer Improvement District (CWSID) is located at 2618 West Pioneer Road, Ogden, Utah, 84404. It provides service for approximately 200,000 people in Weber and Davis counties. The plant was constructed in 1957. The existing treatment facility had a rated capacity of 45 million gallons per day (MGD), using a single-stage trickling filter process. Project upgrades completed in 2011, included construction of a new parallel 30-MGD activated sludge treatment plant, a new headwork's facility and a new raw sludge pump station. Focus was placed on value engineering directed at emerging areas of design where improvements could be made to reduce construction costs without affecting the process design or overall finished product.

The upgrades increased the treatment capacity to 70 MGD, supporting the District's goal of accommodating projected population growth in Davis and Weber Counties until 2025. The facility was also brought into compliance with current Environmental Protection Agency (EPA) and State of Utah regulatory requirements (CWSID, 2011).

3. Literature Review

One of the important parameters is the pH, which is defined as the negative logarithm of the hydrogen-ion concentration (Metcalf et al. 2013). An important environmental parameter, pH indicates if the environment is healthy for the microorganisms in the anaerobic digester. The pH should be around neutral (or pH=7) according to McCarthy (1964), while Turovskiy & Mathai (2006) mentioned that the anaerobic microorganisms are sensitive to changes in pH lower than 6.8 and higher than 7.2. The pH inside the digester should be in the range of 6.8- 7.2 in order to keep the microorganisms in a healthy environment.

Due to the chemical reactions inside the anaerobic digester, the volatile fatty acids like acetic, propionic, valeric and butyric acids may accumulate as a result of a drop in the pH. The drop in the pH may occur because the carbon dioxide ranges between 30-50% of the produced biogas; the carbon dioxide may react with the water and form H2CO3, which leads to a drop in pH.

In case an insufficient buffer is present, the pH is subjected to a sudden drop, and that will affect the anaerobic digester's microorganism groups especially Methanogenesis. Methanogenesis archaea will not be able to convert the hydrogen and acetic acid to biogas and that will cause the accumulation of VFA.

The buffering capacity (alkalinity) of the system is important to avoid a sudden drop in pH. Alkalinity in water and wastewater results from the presence of hydroxide [OH^-], carbonate [CO_3^{-2}], and bicarbonate [$HCO3^-$]. Alkalinity concentration is an important factor for the anaerobic digester; alkalinity in the range between 2000 to 4000 mg/L as

$CaCO_3$ is typically required to maintain the pH at or near the optimum value for the anaerobic digester ((Turovskiy and Mathai 2006).

Another important parameter for the anaerobic digester is temperature. Usually anaerobic microorganisms are sensitive to the temperature in the anaerobic digester. Anaerobic digesters can be operated at different ranges of temperature like mesophilic (30-40°C), or thermophilic (41-50°C) for best results. The important factor is to avoid sharp and frequent fluctuations in temperature in order to keep the methanogen microorganisms working in a healthy environment (Arsova 2010).

Besides the pH and the temperature, the accumulation of the VFA (acetic, propionic, valeric and propionic) may control the process. The VFA is an important mid-product in the process of methane production(Bitton 2005)

Wang et al. (2009) discussed the effects of VFA concentration on methanogen microorganisms and methane yield within anaerobic digester. The results from this study confirmed that, when the highest concentrations of ethanol, acetic and butyric acid were 2400, 2400 and 1800 mg/L respectively, there was no significant inhibition in the activity of the methane formers. However, when the propionic acid concentrations had been increased from 300 to 900 mg/L, an inhibition appeared, and accordingly, the methanogens archaea concentration decreased from 6*107 to (0.6-1)*107 mL-1 when propionic reach the concentration of 900 mg/L (Wang et al. 2009). Gallert et al., 1997 also discussed the effects of VFA concentration on methane yield and methanogen microorganism; these effects demonstrated the accumulation of VFA affects the yield of methane (methane production decreased when the VFA accumulated). The accumulation above 2200 mg/L of the VFA decreased the methane production by 50% at mesophilic temperature(Gallert and Winter 1997).

In the anaerobic digestion process, Chemical Oxygen Demand (COD) usually is the best way to track the energy flow during biological oxidation of sludge; the test uses oxidize agent to oxidize organic compounds to carbon dioxide. COD mass balance can be used to account for the changes in COD during digestion. The COD removed in the anaerobic digester is accounted for by the biogas production as shown in the mass balance equation 1:

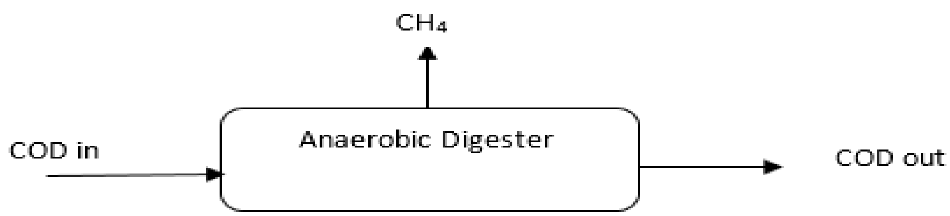

Figure 3. Schematic diagram for the flow through anaerobic digester

COD in – COD out= CH_4 (1)

The COD mass balance equation is able to estimate methane production if other terms were measured.

Equation 1 is used to determine the methane gas production from the anaerobic digester at CWSID after COD removed was measured.(Donoso-Bravo and Fdz-Polanco 2010) studied the steady-state model for the anaerobic digestion of sewage sludge, applying mass balance equation and measuring total COD from the sludge flow. The samples were taken from the influent and effluent side of the four laboratory reactors, using wastewater from a plant in Cape Town, South Africa. The results confirmed that 96, 100, 95, and 99% of the total COD had been recovered for the four lab reactors.

In this paper, the total COD concentrations and volatile solids in municipal (primary and secondary) sludge were monitored, in order to study the anaerobic digester performance at CWSID. Other important parameters were also measured for the same purpose (pH, alkalinity, VFA, and propionic acid). All the analysis and measurements are discussed in full detail.

4. Materials and Methods

In order to monitor the performance of the anaerobic digester operation, influent and effluent sludge samples were taken from a mesophilic digester operating at a 20-day hydraulic retention time. Duplicate influent and effluent sludge samples (ca. 500 milliliters) were analyzed for total solids; VS and COD twice per week using Environmental Protection Agency method (EPA, Method 1684 for total solids and VS measurements and Method 410.4 for COD measurements). All sludge samples were collected in plastic bottles (500 milliliters) and mixed gently by inverting the bottles several times.

The percent total solids (TS%) consist of the solid residue remaining after the sludge sample had been evaporated and dried at 105°C. To measure percent total solids, approximately fifteen (15) milliliters of sample was placed on a pre-weighted fiberglass pad and then heated to 105°C (for 30 minutes) in a CEM microwave instrument (Model CEM001; Matthews, North Carolina). Percent volatile solids (VS%), which is the percentage of the total solids that can be volatilized at 550°C, was measured by taking the total solids sample and placing it in a muffle furnace set at 550°C for one hour (EPA, 2012). The remaining ash was measured and recorded to determine the percent volatile solids. COD of influent and effluent sludge samples was measured using a spectrophotometer (HACH 8000), with accuracy ±5%.

In addition to total solids, volatile solids and COD, effluent sludge samples (ca. 500 milliliters) were taken twice a week to monitor digester pH, alkalinity, and volatile fatty acid concentrations. The pH was measured using a pH meter (Orion 001, Model 230 A-Cole Parmer, Inc. Vernon Hills, Illinois) that was calibrated using pH buffer solutions of 4,7 and 10 (sodium bicarbonate, RICCA Chemical Company). The accuracy of the pH meter was ±0.02 pH units. Alkalinity measurements were conducted according to Standard Methods 2320B using an automated titration system (METER TOLEDO, Columbus, OH) having an accuracy of ± 0.02 milligrams per liter as $CaCO_3$. Prior to the analysis. Biogas generation (cubic feet per minute), percent carbon dioxide, and hydrogen sulfide concentrations in biogas were measured twice per week. Biogas was measured using a gas flow meter (Sierra Instrument Company Model 640S-NAA-L09-M1-E2-P3-V4-DD-5 L Monterey, CA 93940). To measure the concentration of carbon dioxide and hydrogen sulfide in biogas, a one-liter sample of biogas was collected from the digester using a sealed polyvinyl fluoride (PVF) TedlarTM sampling bag. Dragger tubes (model, D-23560, Lubeck, Germany) were used to measure the concentration of carbon dioxide and hydrogen sulfide in the biogas. The accuracy of the dragger tube was ±5% for both kinds of tubes.

To measure volatile fatty acids (VFA) (acetic, propionic, butyric and valeric), 500 milliliter sludge samples were taken from the effluent side of the digester. Total volatile fatty acids were measured using Gas Chromatographic Method number 5560 D (APHA, 2012). From the sample, 200 ml was centrifuged for five (5) minutes. After that, 100 milliliters supernatant liquid was placed in a 500-milliliter distillation flask. Next, 100 milliliters of distilled water was added to the solution along with 0.3 grams of Polytetrafluoroethylene (PTFE) boiling stones and 5 milliliters of 95.9% sulfuric acid. The solution was mixed by inverting the bottle upside down several times, and then 150 milliliters of solution was placed in a 250 milliliter graduated cylinder. The solution was titrated with 0.1N NaOH and expressed as acetic acid content.

Propionic acid was measured in effluent sludge samples two times every week. The sludge samples were collected in a plastic bottle (500 milliliters) and preserved at 5°C. Within 24 hours, the samples were measured for propionic acid using a ThermoFisherTM ICS-5000 chromatograph equipped with an AS18-4um, 4X150mm capillary column and a thermal conductivity detector. The standards used to determine the detection limits for the various acids ranged from 0.5ppm to 2ppm.

5. Results and Discussion

Table 3 shows the results for pH, alkalinity, propionic and VFA respectively during one hundred days of study. The results of the average pH values were 7.31, alkalinity was 4113 mg/L as $CaCO_3$, average propionic acid was 29.38 mg/L, and the VFA average was 65.72±14 mg/L. These results demonstrated the stable performance of the digester at CWSID since all the parameters were under the desired concentration of the effective digester as mentioned in the literature section(Bitton 2005; Metcalf et al. 2013). Also the propionic acid and the VFA were below the critical concentrations that may inhibit the process (900 mg/L and 2000 mg/L respectively) (Kroeker et al. 1979; Wang et al. 2009). Moreover, the average percentage methane was stable at 61.3±4.62%. Which indicates also the stable and effective performance for the digester at CWSID since relatively constant gas produced from the digester and relatively constant accumulation of the VFA at the same time (Kroeker et al. 1979; Metcalf et al. 2013).

The mass balance for COD has been calculated in order to determine the methane gas from COD (CH_4 as a COD) and to compare it with the actual methane gas produced from the digester. Percentage recovery between the theoretical CH_4 which calculated from COD mass balance and actual methane was determined as shown in Table 4. The average percentage recovery was 89.72%, the anaerobic digester was successful in converting the organic wastes (COD) to methane with (~90%) recovery which indicates an active digester performance.

Figure 4 shows the relationship between theoretical (CH_4 as COD) and actual CH_4; linear relationship and high correlation (the regression R^2=0.9892) between the two variables was noticed. The observed data for actual and theoretical CH_4 was transformed to log transformation in order to normalize the data.

Table 3. pH, Alkalinity, Propionic and VFA at CWSID digester

Process	pH	Alkalinity as $CaCO_3$(mg/L)	Propionic (mg/L)	VFA(mg/L)
Day 1	7.40	4275	12.90	26.40
Day 3	7.46	3900	27.54	69.40
Day 8	7.32	3550	25.80	69.11
Day 10	7.25	3892	33.00	55.50
Day 15	7.43	4125	24.96	55.00
Day 17	7.39	4200	15.84	41.60
Day 22	7.21	4450	26.40	52.00
Day 24	7.26	4325	32.64	55.50
Day 29	7.34	4350	41.47	66.20
Day 31	7.30	3825	31.20	69.11
Day 36	7.39	4125	20.40	41.40
Day 38	7.39	3562	24.18	54.40
Day 44	7.30	3992	41.64	86.11
Day 46	7.42	4200	31.20	69.40
Day 52	7.39	4430	45.60	78.23
Day54	7.26	4120	30.60	72.25
Day 59	7.36	4245	24.84	69.40
Day 63	7.37	4075	33.30	80.30
Day 68	7.29	3994	33.00	70.50
Day 70	7.05	4275	22.59	76.98
Day 75	7.34	4170	29.16	78.19
Day 77	7.07	4215	23.64	65.34
Day 82	7.00	4214	30.11	81.18
Day 84	7.35	4200	42.26	80.35
Day 90	7.41	4140	30.18	79.21
Average ± SD	***7.31 ±0.12***	***4113.98±229.14***	***29.38±7.89***	***65.72±14.71***

Table 4. COD in and COD out, Theoretical CH_4, Actual CH_4 and Percentage recovery from the digester at CWSID. SD represents the standard deviation

Process	COD in (mg/L)	COD out (mg/L)	Net COD (mg/L)	Theoretical CH_4 (Ib/d)	Theoretical CH_4 (Ft^3/d)	Actual CH_4 (Ft^3/d)	Percentage Recovery (%)
Day 1	64930	30850	34080	16200	102338	90923	88.85
Day 3	65610	33450	32160	15288	96572	87043	90.13
Day 8	85160	24490	60670	28841	182184	166011	91.12
Day 10	71294	24895	46399	22057	139330	122821	88.15
Day 15	73000	23147	49853	23699	149702	128999	86.17
Day 17	81245	27450	53795	25573	161539	143999	89.14
Day 22	79745	25575	54170	25751	162666	145003	89.11
Day 24	83230	27860	55370	26321	166269	148215	89.23
Day 29	87450	32125	55325	26300	166134	153031	92.11
Day 31	92090	33970	58120	27629	174527	160762	92.12
Day 36	90950	33815	57135	27160	171569	158037	92.10
Day 38	87845	29375	58470	27795	175578	153035	87.16
Day 44	98400	31375	67025	31862	201268	179413	89.14
Day 46	89175	35125	54050	25694	162305	139859	86.17
Day 52	88067	34075	53992	25666	162131	141315	87.16
Day54	85800	28295	57505	27336	172680	157351	91.12
Day 59	77125	23200	53925	25634	161930	145951	90.13
Day 63	81500	22890	58610	27862	175998	158631	90.13
Day 68	68500	28875	39625	18836	118980	127247	93.50
Day 70	84437.5	26925	57512.5	27340	172703	152239	88.15
Day 75	74593	22754.5	51838.5	24642	155664	138762	89.14
Day 77	96580	32393	64187	30513	192745	173725	90.13
Day 82	91885	32916.5	58968.5	28032	177075	159601	90.13
Day 84	91880	31883	59997	28521	177505.85	163128	92.00
Day 90	90905	30831	60074	28557	177733.66	161276	90.74
Average	***83255***	***29141***	***54114***	***25724***	***162285***	***146255***	***89.72***
SD	***9365***	***4029***	***8354***	***2457***	***24914***	***22950***	***1.85***

The conversion factors used for Table 4 are:

1. Theoretical CH_4(Ib/d) = net COD (mg/L) *8.34*Flow (Million Gallons per day)
2. Theoretical CH4 (ft^3/d) = [Theoretical CH4(Ib/d) *0.39*(CH4 L/g)*453.6 g/Ib]/28.3

3. Percentage Recovery (%)= [(Actual CH4 (Ft3/d)/Equivalent CH4 (Ft^3/d)] *100

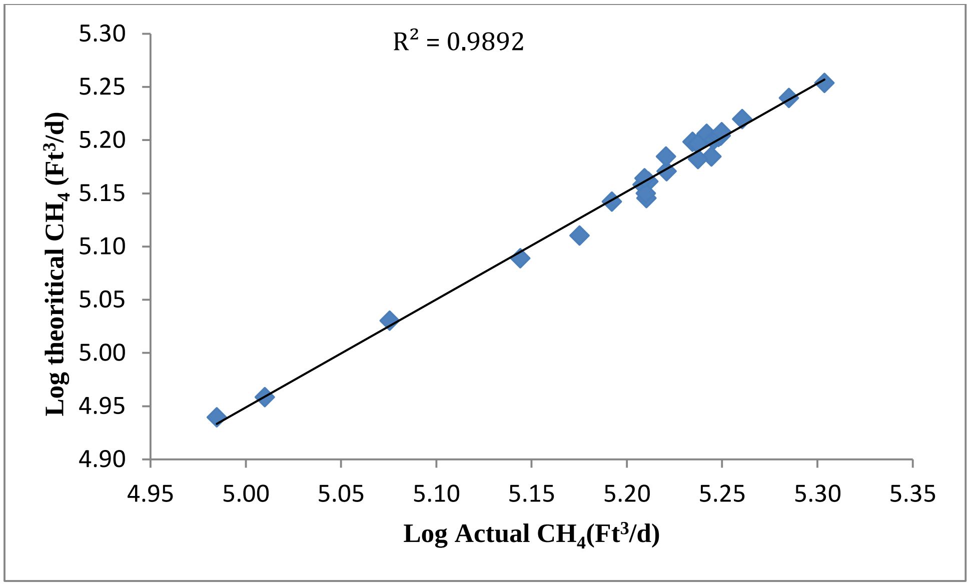

Figure 4. The relationship between theoretical (CH_4 as COD) and actual CH_4

The percentage of VS destroyed (ΔVS) was determined and converted to theoretical CH_4 during the period of study; the results and percentage recovery of methane gas were determined and displayed in Table 3.

Figure 5 shows the relationship between the actual and theoretical CH_4 at the digester at CWSID. The correlation between the theoretical and actual CH_4 was determined after transforming the data (theoretical CH_4 and actual CH_4) to log transformation in order to normalize the data. Strong correlation between the two variables was noticed since the regression (R^2=0.8642).

The variations of the pH, alkalinity, propionic, VFA and COD removal, with time (days) were plotted in order to clarify the daily process of the digester and the relation between all the parameters. The mass balance for the ΔVS was calculated; the equivalent amount of methane gas from ΔVS has been calculated, and the percentage recovery was determined. High percentage recovery was noticed 91.25 %. The relationship between actual and theoretical methane from VS mass balance is plotted in Figure 5.

Table 5. Theoretical CH_4 as VS, Actual CH_4 and percentage recovery from the digester at CWSID. SD represents the standard deviation

Process	CH_4 as VS (L/d)	Theoretical CH_4 (Ft^3/d)	Act CH_4(Ft^3/d)	Recovery %
Day 1	2982435	105386	90923	86.28
Day 3	2853506	100831	87043	86.33
Day 8	4850354	171391	166011	96.86
Day 10	3994021	141131	122821	87.03
Day 15	3935884	139077	128999	92.75
Day 17	4233591	149597	143999	96.26
Day 22	4194233	148206	145003	97.84
Day 24	4579952	161836	148215	91.58
Day 29	4745208	167675	153031	91.27
Day 31	5076446	179380	160762	89.62
Day 36	4703089	166187	158037	95.10
Day 38	4987000	176219	153035	86.84
Day 44	5876765	207660	179413	86.40
Day 46	4621902	163318	139859	85.64
Day 52	4825382	170508	141315	82.88
Day54	4533550	160196	157351	98.22
Day 59	4911462	173550	145951	84.10
Day 63	4621902	163318	158631	97.13
Day 68	3726590	131682	127247	96.60
Day 70	4396687	155360	152239	97.99
Day 75	4848107	171311	138762	81.00
Day 77	4963958	175405	173725	99.04
Day 82	5392226	190538	159601	83.76
Day 84	5187218	183294	163128	88.99
Day 90	4678750	165327	161276	97.55
Average	***4548808***	***160735***	***146255***	***91.25***
SD±	***675158.30***	***23857.18***	***22950.07***	***5.81***

1. Theoretical CH_4 as VS (ft^3/d) = [Theoretical CH_4(Ib/d) *0.39*(CH_4 L/g) *453.6 g/Ib]/28.3

2. Percentage recovery (%)= [(Actual CH_4 (Ft^3/d)/Equivalent CH_4 Ft^3/d)] *100

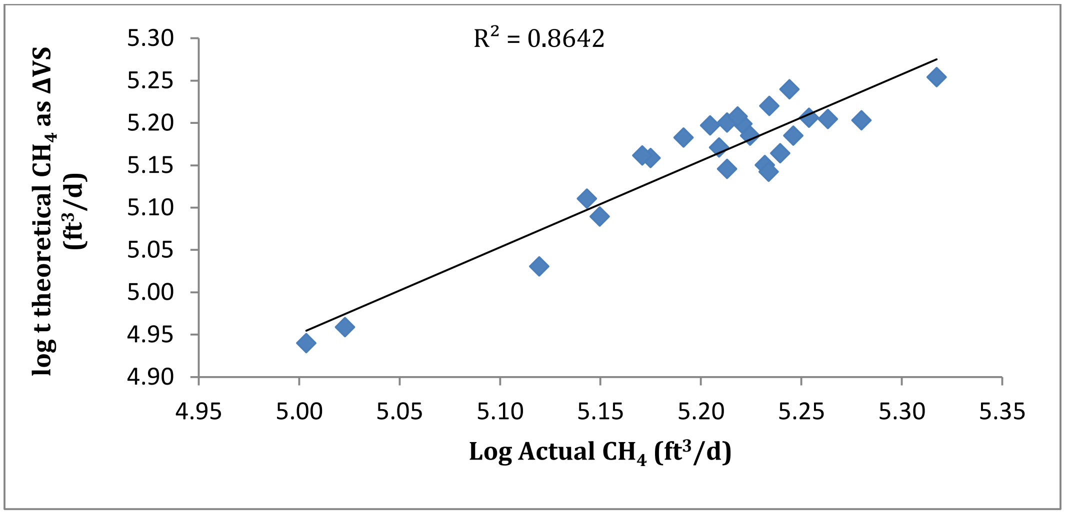

Figure 5. The relationship between theoretical (CH_4 as ΔVS) and actual CH_4

Figure 6, shows that, there was no significant fluctuations noticed for the monitored stability parameters (pH, alkalinity, propionic acid and COD) over time. All parameters vary within the recommended range for each parameter (the recommended range for each parameter was mentioned in the literature review section). pH is considered neutral, and the alkalinity results reflected strong buffering capacity to the change in pH inside the digester. Moreover, stable variation in both VFA and propionic acid within the period of time was noticed, which demonstrates the stable rate of converting these intermediate products to acetic acid and hydrogen. The stable rate of conversion keeps the dynamic relationship between the acidogenesis bacteria and the methaongenesis in stable status and rate.

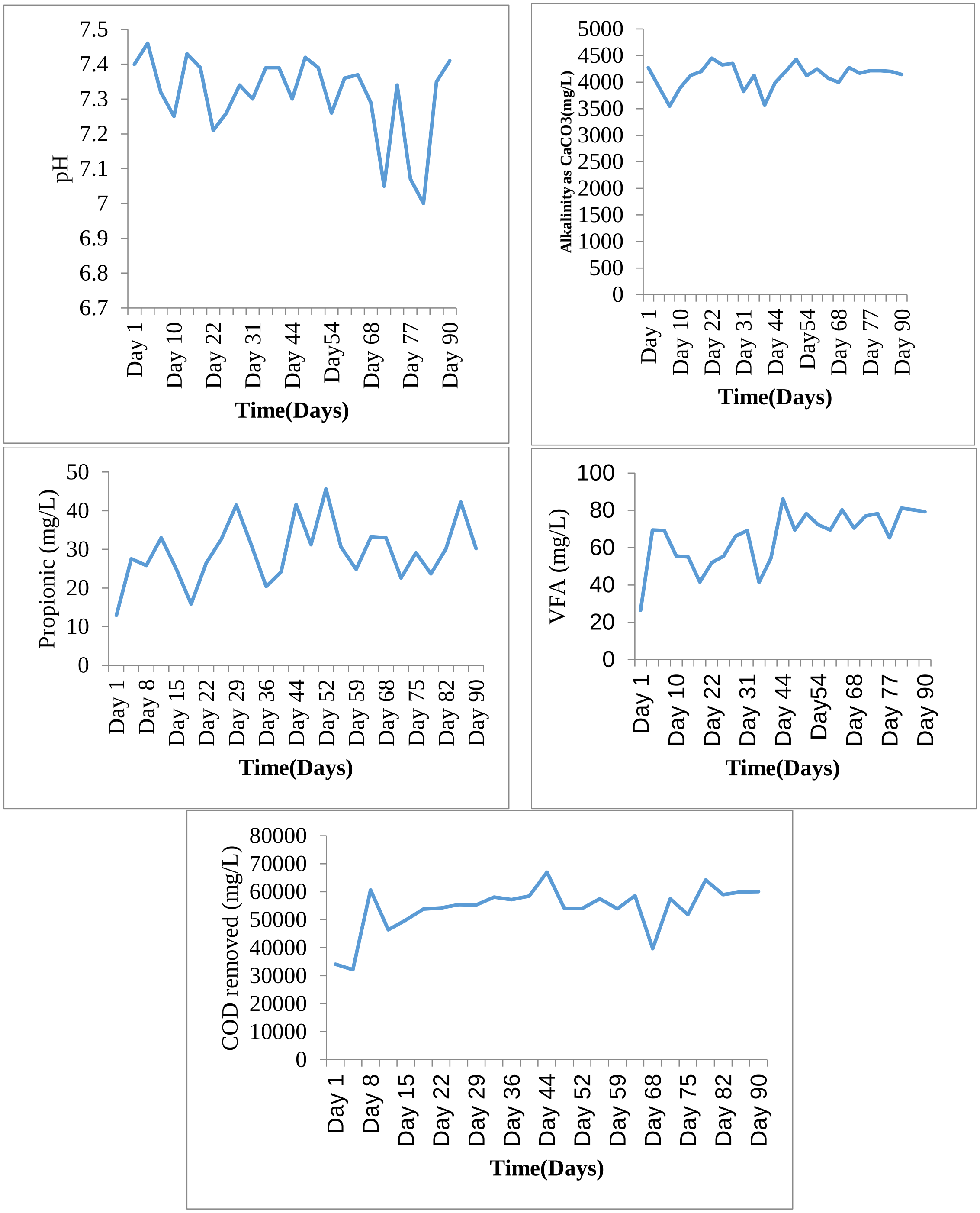

Figure 6.The variation of pH, alkalinity, Propionic acid, VFA and COD with time at CWSID digester

The digester is considered to be at a stable steady-state condition because it was operating at or near the controlled and fixed-variable designed levels(Kroeker et al. 1979; Metcalf et al. 2013; Turovskiy and Mathai 2006). Furthermore, gas production rates were relatively constant during the period of study as shown in Figure 4. Based on the stable and active digester at CWSID, a stability index function was determined in order to define the anaerobic digestion process in an easy method that can reduce the effort and time of monitoring all the digester's parameters daily at the facility. The rate between methane gas produced from the digester and destroyed volatile solids (ΔVS) in liter per gram was determined during one hundred days of study as shown in Table 6. Daily rate of (0.40±0.03) L/g has been determined, which demonstrates that stability is achievable as long as the constant rate of 0.4 L/g is maintained.

The rate of CH_4/ΔVS (0.40 L/g) can be used as a stability index to indicate the stability process of the anaerobic digester as applied at CWSID since all the other parameters indicates stable and effective digester. The destroyed VS and the methane gas were monitored daily in most of the wastewater facilities, these two parameters only (ΔVS and CH_4) can be used to evaluate and monitor the stability process for the digester.

Figure 7 shows the relationship between the stability index (L/g) and propionic acid. Inverse proportion between the two variables was noticed. An increase in the propionic acid will affect the rate of methane gas produced per ΔVS (L/g). Methanogenesis archaea may get stressed partially when propionic acid accumulates and reaches 45 mg/L, which causes the low stability index readings as shown in Figure 7.

Table 6. Stability index ($CH_4/\Delta VS$ (L/g)) and the propionic acid concentration from the digester at CWSID. SD represents the standard deviation

Process	$CH_4/\Delta VS$(L/g)	Propionic (mg/L)
Day 1	0.37	12.90
Day 3	0.38	27.54
Day 8	0.43	25.80
Day 10	0.38	33.00
Day 15	0.41	24.84
Day 17	0.42	15.84
Day 22	0.43	26.40
Day 24	0.40	31.200
Day 29	0.40	41.64
Day 31	0.39	30.60
Day 36	0.42	20.40
Day 38	0.38	24.18
Day 44	0.38	42.26
Day 46	0.38	31.20
Day 52	0.38	45.60
Day54	0.36	30.18
Day 59	0.43	24.96
Day 63	0.37	33.30
Day 68	0.43	32.64
Day 70	0.43	22.59
Day 75	0.36	29.16
Day 77	0.44	23.64
Day 82	0.37	33.6
Day 84	0.38	41.47
Day 90	0.43	33.00
Average	***0.40***	***29.51***
SD±	***0.03***	***7.93***

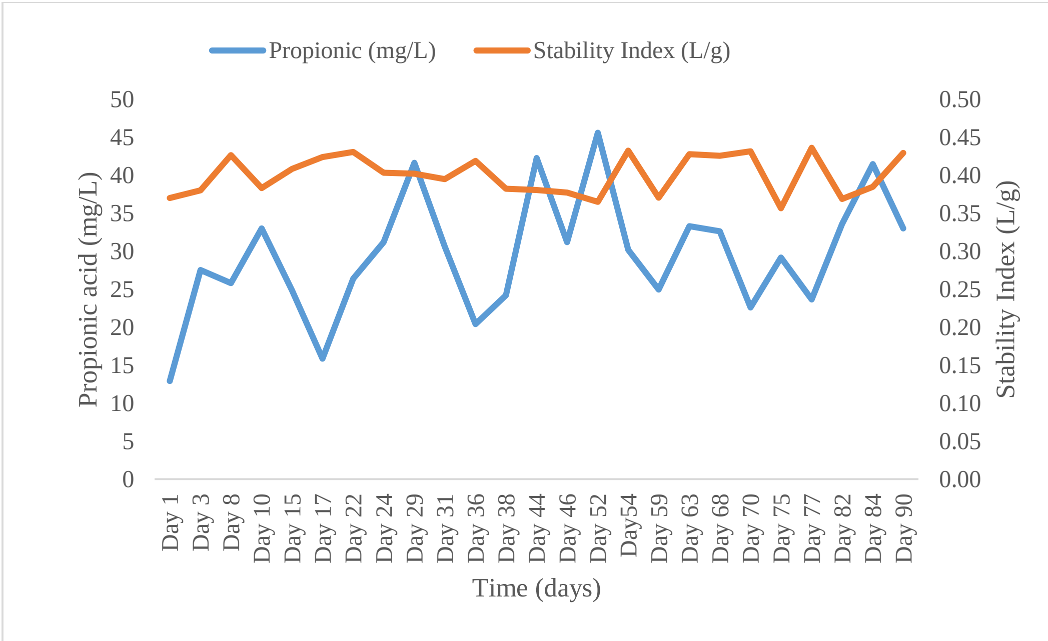

Figure 7. The relationship between the stability index ($CH_4/\Delta VS$) and propionic acid during the time of study

6. Conclusion

In this research, full-scale anaerobic digester stability at CWSID was tested and monitored during one hundred days of study. The municipal primary sludge mixed with secondary sludge (25% primary sludge and 75% secondary sludge) was characterized as COD.

Snap shots of the anaerobic digester parameters during the period of study were monitored. The COD mass balance was applied to the anaerobic digester in order to study its stability and its capability of producing methane gas. The anaerobic digester mass balance showed promising results in terms of wastewater treatment and energy production. There was a 10% loss of the methane gas (the best gas recorded was 90% of the organic wastes loaded). Mass balance of ΔVS was calculated, and 91% recovery was possible. Essentially, the monitored parameters for the anaerobic digester were pH, alkalinity, VFA, and propionic acid. All the results confirmed a stable performance for the anaerobic digester.

Finally, at mesophilic temperature and stable steady state performance, anaerobic digester stability has been defined as a constant rate of methane produced per substrate of ΔVS (average rate = 0.40 L/g). This definition (the stability index) can be used as an easy and inexpensive method to define and examine the anaerobic digestion process stability. This research indicates that the stable anaerobic digesters are a good source of energy recovery for the wastewater treatment plants.

Since defining "stability" was considered an initial problem, this research also furthered the ability to define or redefine it more simply by using the consistent results of this study.

7. Acknowledgements

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CHAPTER 3

Modifying the ADM1 Model to Predict the Operation of an Anaerobic Digester Co-Digesting Municipal Sludge with Bakery Waste

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Abstract

The Anaerobic Digestion Model Number1 (ADM1) was modified in order to predict accurately the impact of co-digesting bakery waste (BW) with municipal sludge (MS). BW is an industrial waste (300,000 gallons per day in USA) that contains a high concentration of organic matter (carbohydrates, low lipids and non-detected proteins). BW is an easily biodegradable substrate for creating a favorable microorganism growth environment, which enhances the biogas production needed for wastewater facilities. The modified ADM1 reasonably predicted changes in pH, volatile fatty acids (VFA), propionic acid and methane gas production. The ADM1 outputs were compared to experimental batch scale reactor results of actual BW addition percentages in order to validate the model. Stability of the digestion process was achieved until the ratio range of 37-40% BW: 60-63% MS, and the digestion processes were inhibited at higher ratios of BW. This research provides an alternative to BW management through utilizing the BW to enhance methane production.

1. Introduction

The anaerobic digestion process is one of the oldest biological process technologies utilized by mankind. The process was first used for food and beverages production, and then developed in the last few decades for wastewater sludge stabilization.

One of the main advantages of the anaerobic process is the high organic loading and low sludge production combined with the amount of energy produced (Turovskiĭ and Mathai 2006).The energy produced from the process is sufficient that it could potentially replace fossil fuel sources as an alternative renewable energy option. The anaerobic digestion process is complicated since it involves many chemical, biological, and physical interactions that must be balanced within the ecosystem.

Stability of anaerobic digestion is an important for scientists and engineers. Changes in the digester environment may affect the stability of the process and the consequences of failure are substantial in terms of regulatory compliance, environmental degradation, and economic impact. Failure of the digester will negatively affect sludge treatment; also, the restart of the digestion process in case of failure is prohibitively expensive(Bitton 2005)

Mathematical modeling reduces the failure risks associated with the anaerobic process; computer models can simulate the process and predict outcomes, thereby helping to reduce the risk of imbalance in the digestion process (Burton 2004; Gary AMY 2008). In this research, the Anaerobic Digestion Model Number1 (ADM1) has been used to simulate the situation of co-digestion bakery waste (BW) with municipal sludge (MS).

There are reports on anaerobic co-digestion of different kinds of industrial waste with sludge (Callaghan et al. 1999; Fountoulakis et al. 2010; Silvestre et al. 2011; Ye Chen 2007; Zhu et al. 2008). However, a specific lack of knowledge exists about the co-digestion of BW (cookies, cakes, and pies) with MS and its potential impact on anaerobic process stability. Furthermore, using the ADM1 model to study and predict the impact of BW mixed with MS for anaerobic digestion, and determining the failure point of the anaerobic digestion process has not been studied or reported.

2. Background

2.1 Stability of the Anaerobic Digestion

While anaerobic digestion is an attractive method for pollution control and energy recovery (Burton 2004), many factors may affect the balance between microorganisms or inhibit them in the anaerobic digester; for example, changes in temperature, retention time (related to loading), pH and toxic materials (Bitton 2011). Inhibition of the available microorganisms will affect the stability of the digester and may prevent it from being widely commercialized (Dupla et al. 2004) for some substrates. Failure to maintain the balance between the acid formers and the methane formers is the main reason for digester instability (Demirel 2002).

Researches have been done to try to enhance methane gas production during co-digestion of food waste by combining it with other organic matter (Fang et al. 2011; Jiang et al. 2013; Kabouris et al. 2009; Kabouris 2008; L. Martín-Gonzáleza 2010; Long et al. 2012). Wastes from food processers are high in organic matter and thus resulting in high methane gas production, but this same organic material can also inhibit anaerobic microorganisms (Chen et al. 2008). For example, co-digestion of certain food wastes such as meat waste will increase the accumulation of ammonia and volatile fatty acids (VFA); these two substances are potent inhibitors to anaerobic microorganisms in specific concentrations (Kayhanian 1999).

Monitoring the digester parameters such as pH, VFA (acetic, propionic, valeric and butyric), and hydrogen is important; those parameters are used as an early indicator to discover any undesirable inhibition in the microbial community, and to avoid instability of the digester. Accumulation of the VFA inside the digester may control the process and the accumulation of propionic acid in the range between 300- 900 mg/L will result in chronic inhibition of the necessary microorganism environment (Wang et al. 2009). Monitoring daily flow of biogas (Q) and the percentage of methane gas (CH4) are important to ensure a healthy environment for microorganisms in an anaerobic digester. These parameters can be used to evaluate the efficiency of a co-digestion process for enhancing biogas from a wastewater treatment facilities' digester. (Bitton 2011; Burton 2004; Demirel 2002; Henze 2008; Jiang et al. 2013; McCarty 1973; Turovskiĭ and Mathai 2006).

2.2 Bakery Waste

The bakery industry is one of the major food industries throughout the world. Bakery products are categorized as bread, bread rolls and pastry products including cakes, donuts, biscuits, and pies. There are almost 7,000 bakery operations in the USA producing approximately 300,000 gal of wastewater per day (Lawrence K. Wang 2006). BW is rich in carbohydrates and low in lipids and proteins (80% carbohydrates, 20%

lipids and non-detected proteins). The BW is generated from cleaning operations (equipment and floor); the waste is collected into touts (300 gallons per tout) and transported to landfill application (based on information collected from CSM Bakery Products, Ogden, UT). The digesting of BW with MS will minimize the need to landfill BW products and will enhance the biogas production inside the wastewater facilities.

2.3 Model Description

The ADM1 model was established by the International Water Association (IWA) Task Group for mathematical modeling of the anaerobic digestion process(Batstone et al. 2002). ADM1 is a mechanistic model that has open structure, common nomenclature integrating biokinetics with association-dissociation, gas–liquid transfer, and cellular processes involving hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The model uses a large number of constants and coefficients in order to describe the physical-chemical reactions.

Organic matter is characterized according to its Chemical Oxygen Demand (COD) in the ADM1 model. The model applies some variables to describe the behavior of soluble and particulate components. The COD entering the digester is defined as biodegradable and non-biodegradable organic matter. Usually it is a challenge to estimate the percentage of these parameters since most of the time sludge COD is not reported (Parker 2005). However, the IWA group does not provide clear information on how the fraction of carbohydrates, proteins and lipids can be divided for MS (Shang et al. 2005). Sludge composition based on COD, may contain 35% inert, 20% proteins, 20%

carbohydrates, and 25% lipids. Accordingly, the COD in this study was divided into the ratios shown in Figure 8

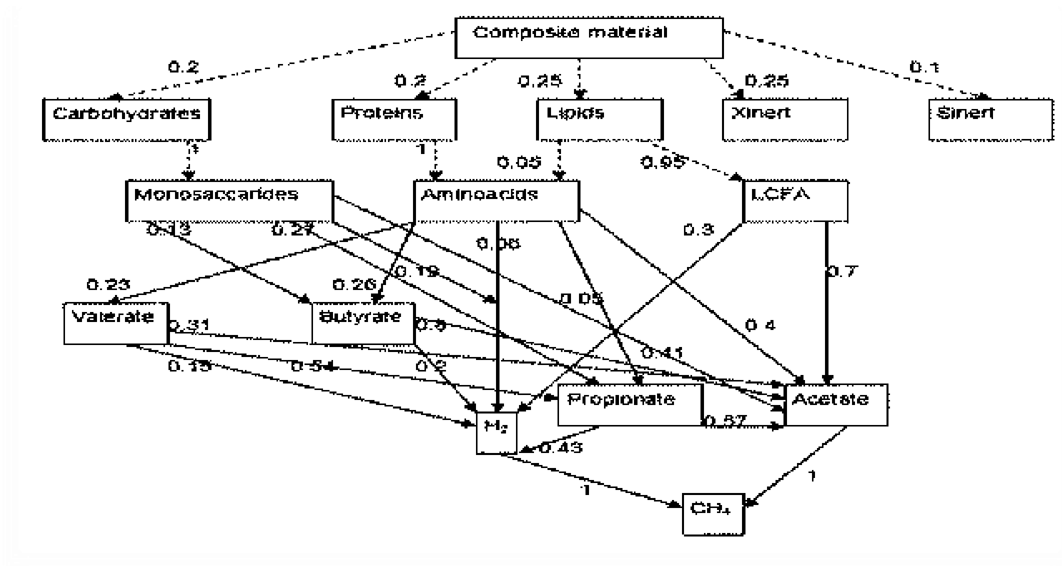


Figure 8.The COD flux for sewage sludge adapted from (Batstone et al. 2002)

Figure 8, the boxes represent products, numerical values represent COD fraction, and arrows represent the direction of mass balance. MS consist of 0.65 as biodegradable organic matter like carbohydrates, proteins and lipids, while 0.35 of the MS is non-biodegradable organic matter. The non-biodegradable MS includes both particulate (Xinert), and soluble (Sinert) materials. Bacterial reactions degrade the complex organic to simple organic matter, then to an intermediate product like volatile fatty acids (Acetate, Propionate, Butyrate, and Valerate). Finally, Methanogenesis archaea converts acetate and hydrogen to methane gas (Batstone et al. 2002).

3. Objectives

The objectives of this research can be subdivided into the following categories:

3.1 Modify and validate an existing mathematical model (ADM1) to be used for BW co-digestion purposes.

3.2 Use the modified ADM1 model to simulate and study the changes in the digester's behavior, and predict the increase of methane gas due to the injection of BW.

3.3 Use the modified model to determine the imbalance point of the digester due to BW mixed with MS.

3.4 Draw conclusions for further research and use of both the modified model and the process of utilizing BW itself.

4. Materials and Methods

The code of the ADM1 was written using R programing software(Team 2015) to describe all the processes and the mathematical dynamic equations that used in ADM1 model.

The ADM1 model using R programing software was applied to a full-scale anaerobic digester at Central Weber Sewer Improvement District (CWSID), Ogden, Utah. Sludge samples for measurements of pH, COD, alkalinity, Total Kjeldahl nitrogen (TKN), ammonia NH3, total solids (TS), volatile solids (VS), and VFA were collected from the anaerobic digester at CWSID; the results are displayed in Table 7. The full-scale digester was monitored for 4 months (June – October 2014) .The standard methods for the examination of wastewater were used for the analysis of each parameter (APHA 2005).

Gas samples were also collected from the full-scale anaerobic digester at CWSID in order to measure the methane gas, carbon dioxide gas, and hydrogen gas content of the biogas by volume. The volume of the digester at CWSID was 5230 m^3 operated under mesophilic temperature (95-98° F) with a retention time of 20 days. The sludge at CWSD was 75% secondary sludge and 25% primary sludge.

BW samples were collected from CSM Bakery Products, Ogden, UT for 4 months (December- April 2015); the characteristics of the BW are displayed in Table 7.

Co-digesting of BW with MS was done in fully-mixed batch scale reactors at the Utah Water Research Laboratory (UWRL), Logan, Utah. Ratios of mixing BW with MS based on total COD were done at 10%, 20%, 30%, 35%, 36%, 37% ,40%, 42%, 44% BW. BW was added and mixed to the MS in the batch reactors; twelve 500 milliliters glass batch reactors were used. For each ratio of BW, the reactors experiment was triplicated in three identical reactors. The reactors were well-mixed using automatic shakers (Lab Line Instrument Company, Melrose Park, Illinois); the speed of the shakers were scaled at number 2. The reactors were placed in incubator, the operating temperature of the incubator was 97° F. Each experiment was conducted for 30 days, the retention time of the experiment was 18 days, and the feeding was conducted once a day. The volume of the daily biogas produced from the reactors was measured using Lab Glassware Pyrex manometer 50 ml. The gas was collected in small disposable syringes (monoject Syringe 60 ml). Methane and carbon dioxide content were measured using an Agilent gas chromatograph 6890 GC, RT-M sieve 5A Plot capillary column (Restek) (Agilent, Santa Clara, CA). The pH was measured using Fisher Scientific pH meter (XL 25 Dual channel). The samples were collected from the solution to measure the VFA and propionic acid using EPA method number 1694 M.

The ADM1 was modified to better predict performance while co-digesting BW with MS; the coefficient parameters of the model were modified based on the chemical composition of MS and BW as shown in Table 1. The model was validated and tested using the results from the batch scale experiments in each stage.

5. Results and Discussion

5.1 Stage 1: Modeling of Full-Scale Digester

The ADM1 model was run to predict the parameters pH, VFA, propionic acid, biogas Q (L/d), methane gas (L/d) and hydrogen gas. The first run of the model assumed that the COD is divided to 20% carbohydrates, 20% proteins and 25% lipids, while 35% of the COD was assumed as inert (non-biodegradable) as shown in Figure 8. For the initial run, values for MS kinetic parameters recommended by Batstone and Keller, 2002 were used in this model.

The model outputs were compared to the observed results from the full-scale digester at CWSID.

Figures 9–12 show the comparison between predicted and observed parameters for the MS before adding BW to the digester.

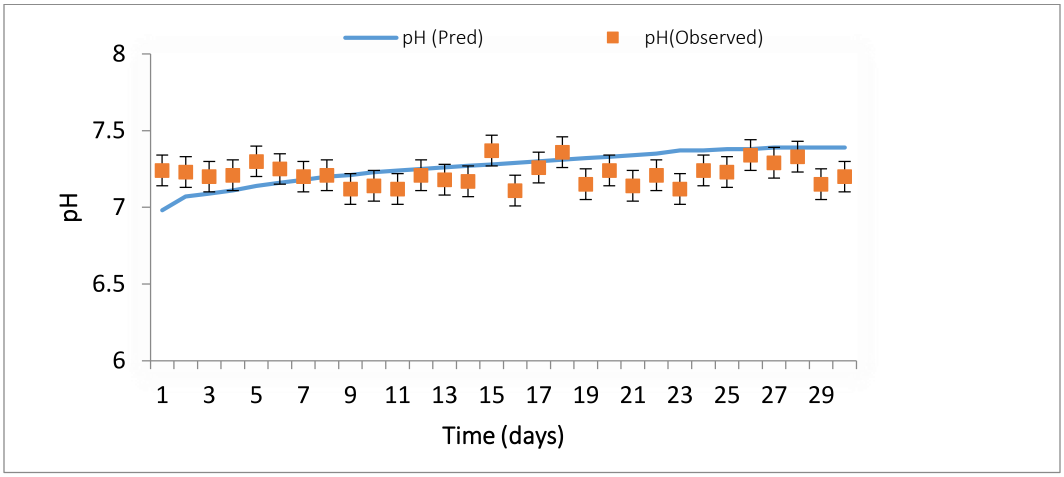


Figure 9. Comparison between predicted and observed pH (Error bars = Standard Deviation)

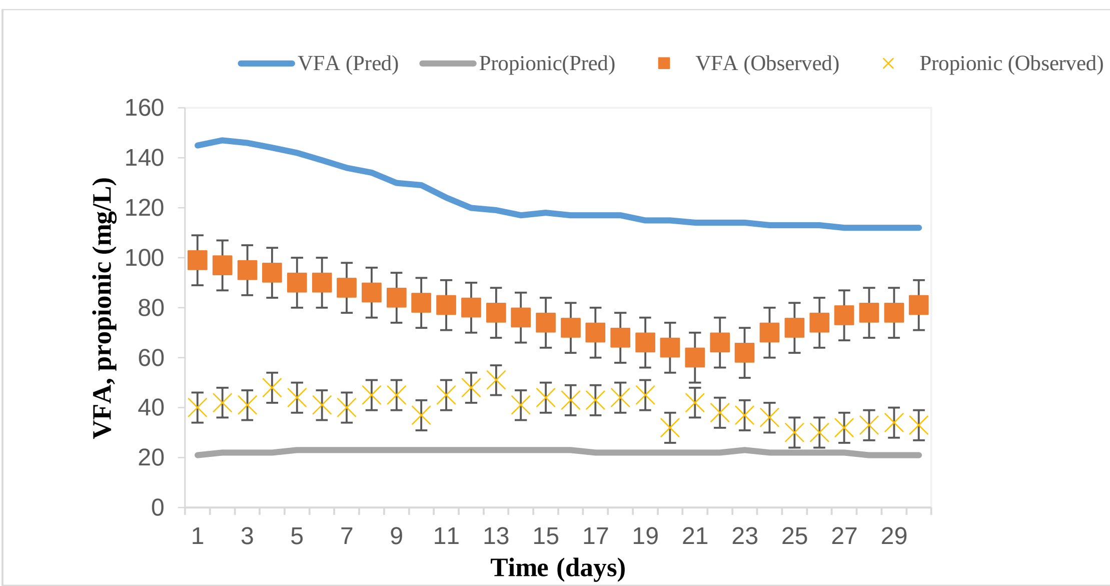


Figure 10. Comparison between predicted and observed VFA and propionic acid (Error Bars = Standard Deviation)

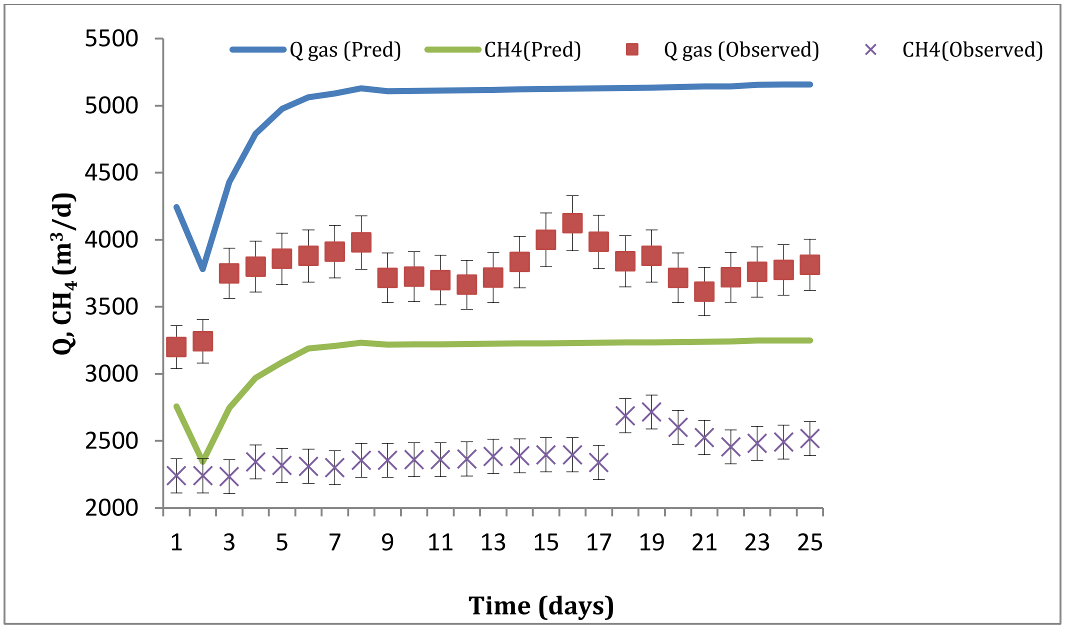


Figure 11. Comparison between predicted and observed Q and CH_4 (L/d) (Error Bars = Standard Deviation)

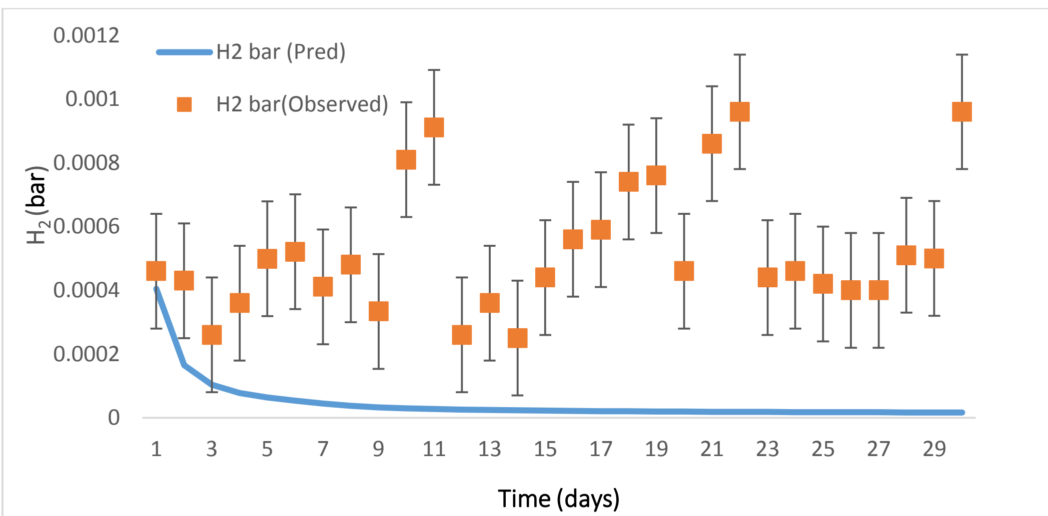


Figure 12. Comparison between predicted and observed H_2 (Error Bars = Standard Deviation)

The model successfully predicted pH values as shown in Figure 9. The values for pH varied between 7–7.35 which indicates a healthy environment for the digester's microorganisms. The model's prediction for the VFA concentration was relatively overestimated especially between days 19 to 24 as shown in Figure 10.

Figure 11 shows the results for observed and predicted biogas and methane gas; the model results overestimated both variables. On the contrary the predicted hydrogen values were underestimated as shown in Figure 12. The model underestimated the hydrogen probably because of the hydrogen coefficient in the model needs to be adjusted.

The observed daily variations in all the monitored parameters were as expected since the samples were taken from a functioning, full-scale commercial digester. On the other hand, the predicted parameters and biogas from the ADM1 model didn't show much variation compared to the observed because the values were based on average inputs for COD, flow, retention time and temperature.

Even though the ADM1 model accurate predictions reflected the trends and general performance of the full-scale digester for the MS (Figure 9–12), the model could not accurately predict the situation of mixed MS and BW. The mechanisms of degradation of carbohydrates, proteins and lipids are not the same in each case; therefore, the model kinetic parameters were modified to reflect the case of mixed MS with BW as discussed in stages 2 to 5.

Stage 2: Adding BW to MS
10 % BW: 90% MS

Initially, BW was added at a rate of 10% of the total digester COD for an average of 28 days. Kinetic parameters in the model were modified to take into account the co-digestion of MS and BW to be more appropriate for the mix of both substrates. The model coefficients for carbohydrates, proteins and lipids were changed to reflect the changes in the digester environment (Table 8). Adding BW was expected to enhance methane gas production from the anaerobic digester because BW is composed of easily biodegradable organic matter. The results are shown in Figures 13–15 for 10% BW.

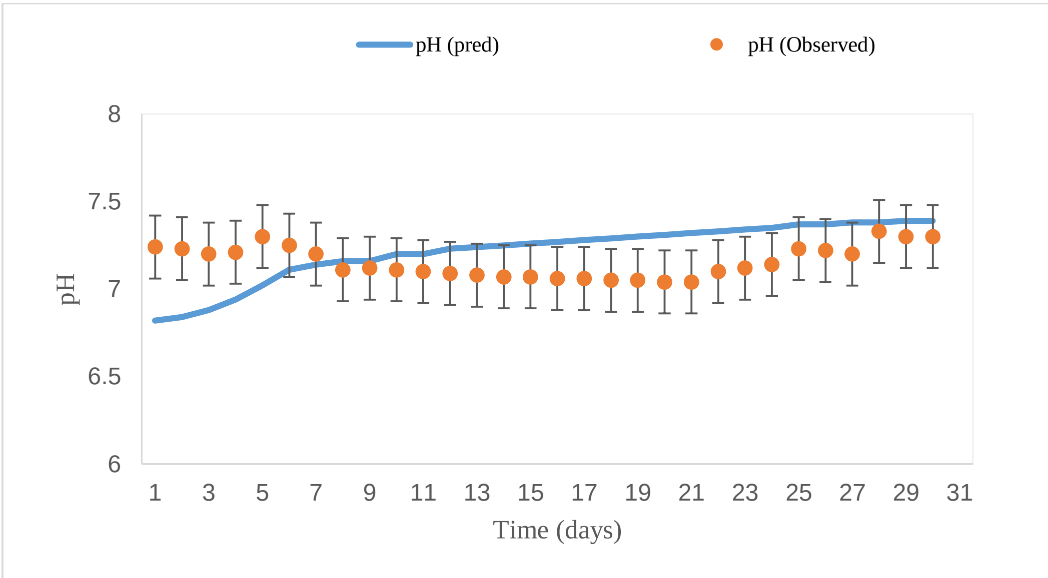


Figure 13. Comparison between predicted and observed pH- 10% BW (Error Bars= Standard Deviation)

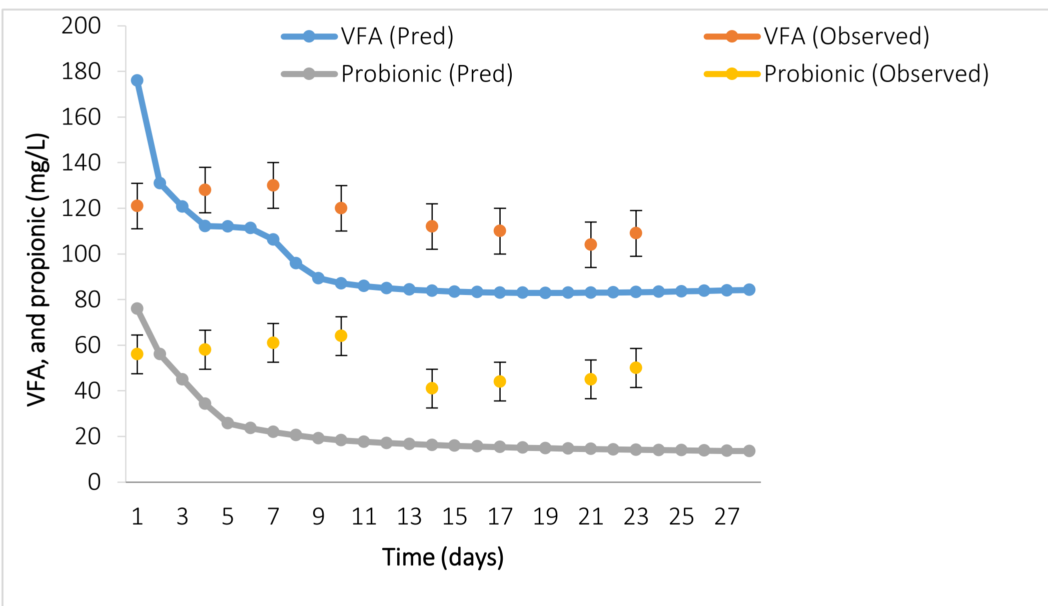


Figure 14. Comparison between predicted and observed VFA, Propionic acid-10 BW (Error Bars= Standard Deviation)

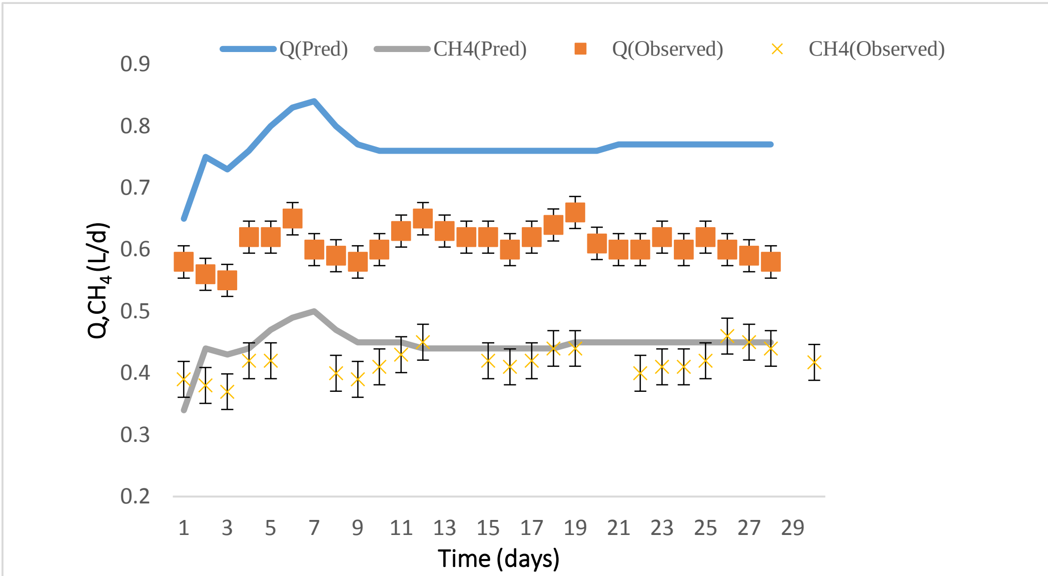


Figure 15. Comparison between predicted and observed Q and CH_4- 10% BW (Error Bars= Standard Deviation)

The model accurately predicted the changes in pH (Figure 13), the pH results were within the range (6.5-7.5) that indicates a healthy environment for the microorganisms. The model predicted changes in VFA (with propionic acid reported separately) (Figure 14). Based on the model outputs, the concentration of the VFA was 176 mg/L during the period from day 1 to 5 then dropped to 87 mg/L on day 10, and ended with 83 mg/L for the rest of the days. The propionic acid concentration was 76 mg/L on day 1 and dropped to 14 mg/L by day 22. This indicates that monitoring the digester in the first 10 days of adding BW is critical because the most significant changes in the digester environment and microorganisms occur during that time. The digester probably needs 10 days to acclimate (the adaptation of the microorganisms with the new substrate). This was also supported by the observed results of the batch reactor; the statistical analysis for observed and predicted data are shown in Table 9.

The model overestimated the biogas produced in this stage, while the predicted methane gas was close to the observed (Figure 15). The model estimated the methane percentage content around 58% of the total biogas, while the observed methane gas was found to be 69% of the total biogas. Therefore, the eventual stable performance of the digester after the 10% BW addition indicated that the digester can accommodate at least this much added BW.

Stage 3: Adding BW to MS
20 % BW: 80% MS

Figures 16–18 show predicted and observed changes in the digester when 20% BW as COD was added to the batch reactor scale. The predicted values for pH, VFA, propionic acid, biogas, and methane gas from the model remained within an acceptable range (±10%). Statistical results are shown in Table 9 for observed and predict values of each parameter (pH, VFA, Q and CH_4). In this stage, there was no indication of inhibition or toxicity to the microorganisms because the pH values were found to be neutral. VFA and propionic acid were less than the critical concentrations (2000 mg/L, 900 mg/L respectively). Therefore, 20% of BW was acceptable for the digester optimum performance.

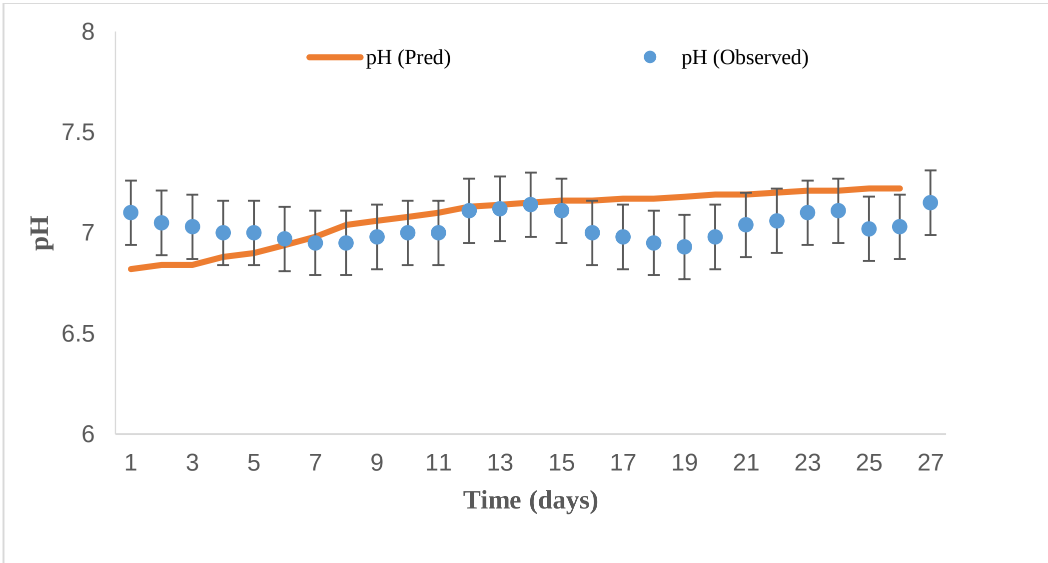


Figure 16. Comparison between predicted and observed pH- 20% BW (Error Bars= Standard Deviation)

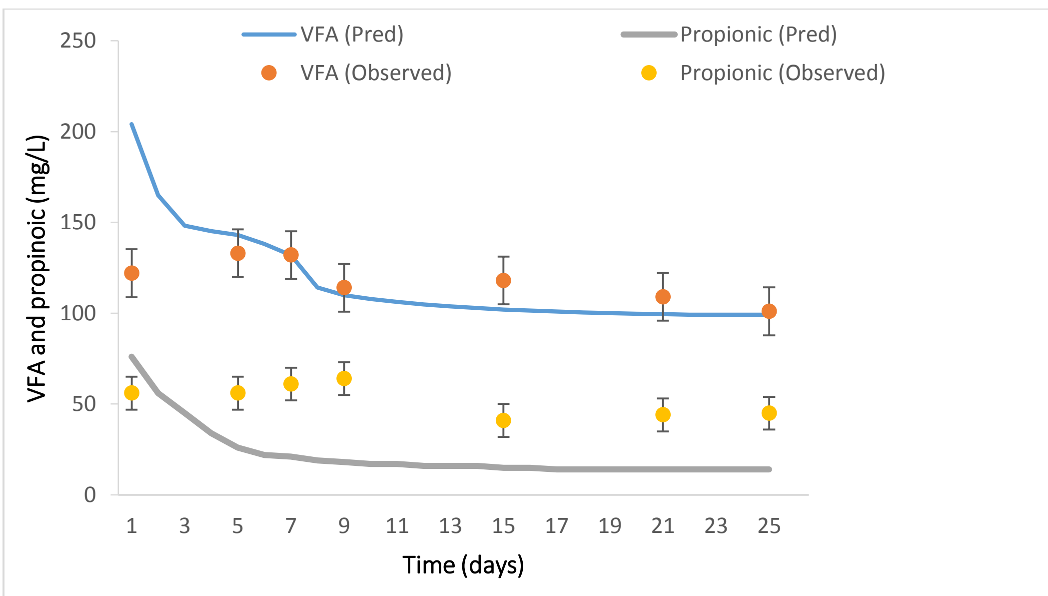


Figure 17. Comparison between predicted and observed VFA and propionic acid- 20% BW (Error Bars= Standard Deviation)

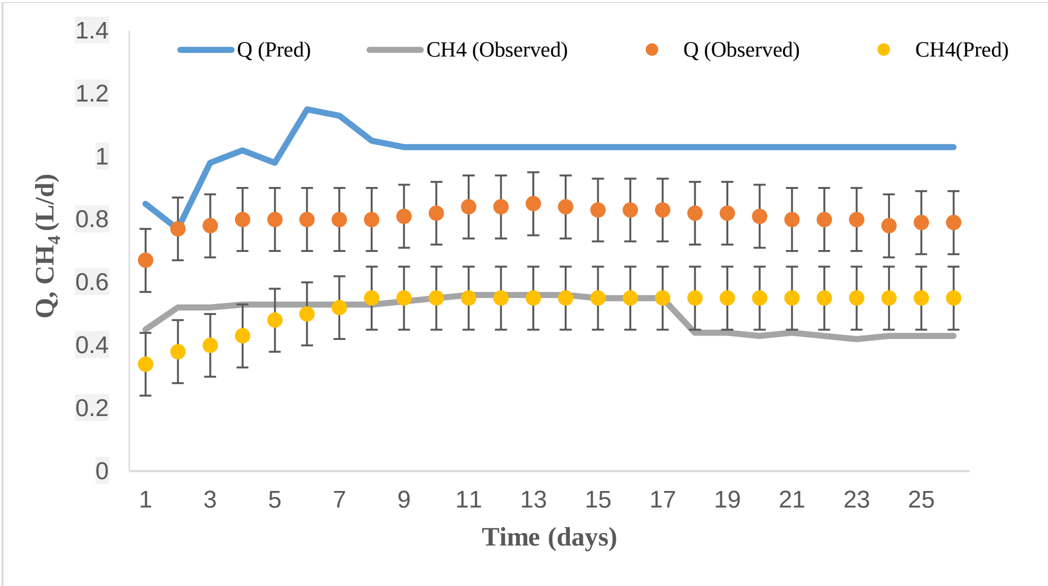


Figure 18. Comparison between predicted and observed Q and CH_4 - 20% BW (Error Bars= Standard Deviation)

Stage 4: Adding BW to MS

30 % BW: 70% MS

At this stage, the BW load was increased to 30% based on COD and the stability parameters were monitored to evaluate the digester behavior with the increase in the BW percentage. The pH values were low for the first 4 days; then the pH values returned to neutral. VFA and propionic acid concentrations were below the critical concentrations for the microorganisms (2000, 900 mg/L). The model was able to predict the methane gas in acceptable range as shown in Figure 21; the statistical analysis for the comparison between predicted and observed are shown in Table 9. Figures 19 – 21 show the results with 30% BW.

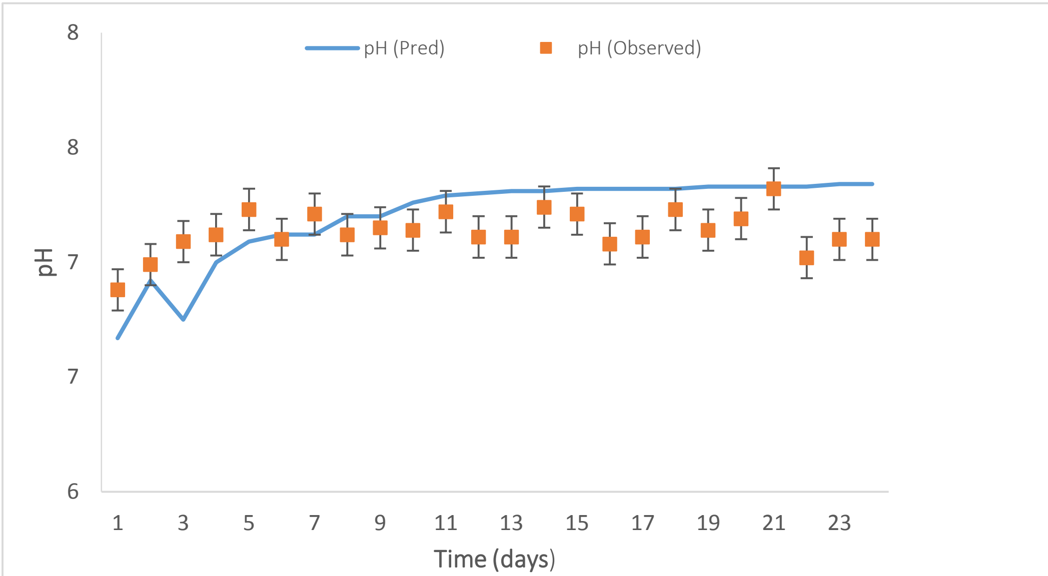


Figure 19. Comparison between predicted and observed pH- 30% BW

(Error Bars= Standard Deviation)

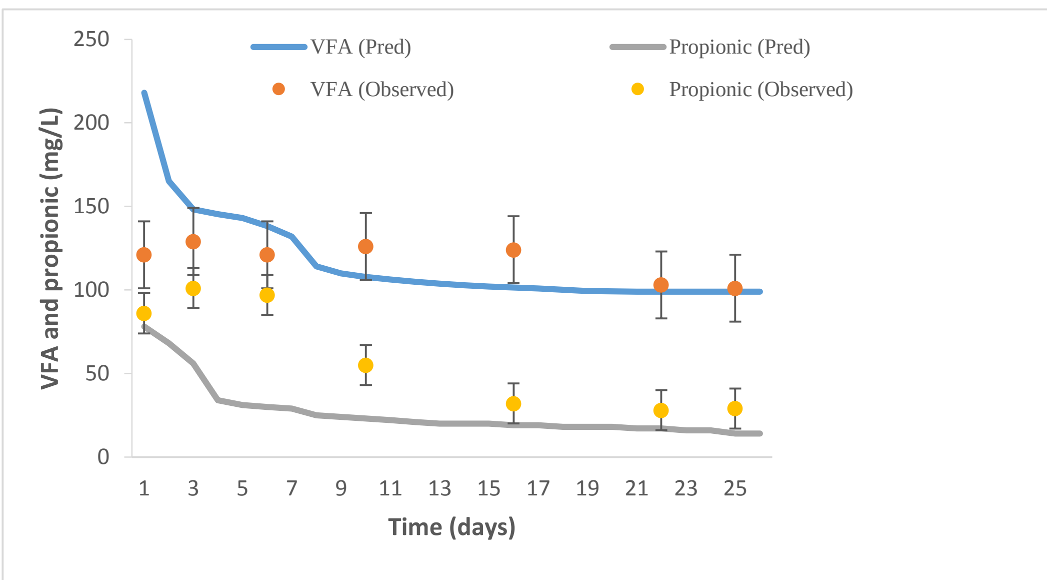


Figure 20. Comparison between predicted and observed pH-30% BW

(Error Bars = Standard Deviation)

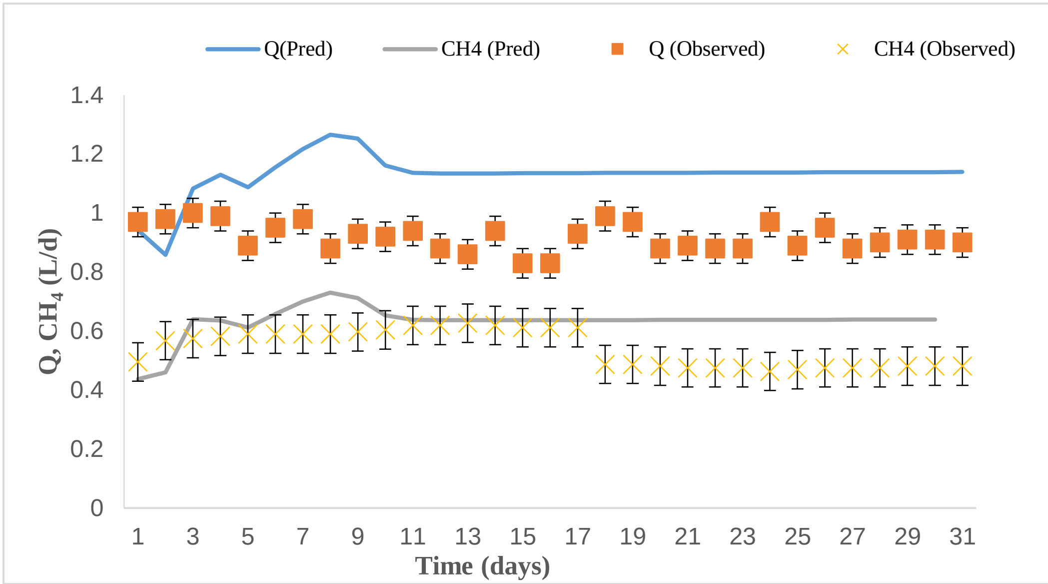


Figure 21. Comparison between predicted, observed Q and CH_4- 30% BW (Error Bars= Standard Deviation)

The Figures (22–24) show the variation of pH, VFA, and methane gas for all the stages when no BW added and with 10%, 20% and 30% of BW addition to municipal sludge.

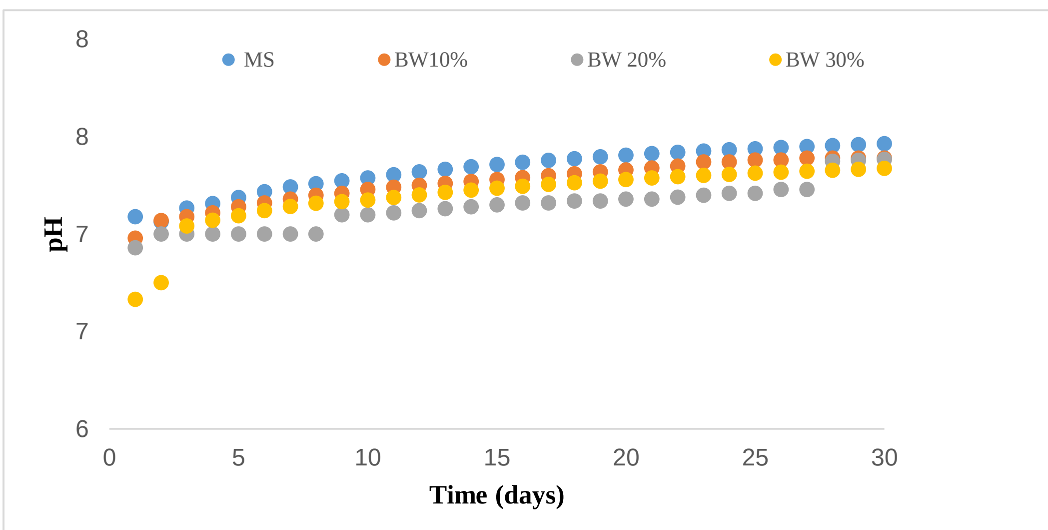


Figure 22. The variation of pH with time (0%, 10%, 20% and 30% BW)

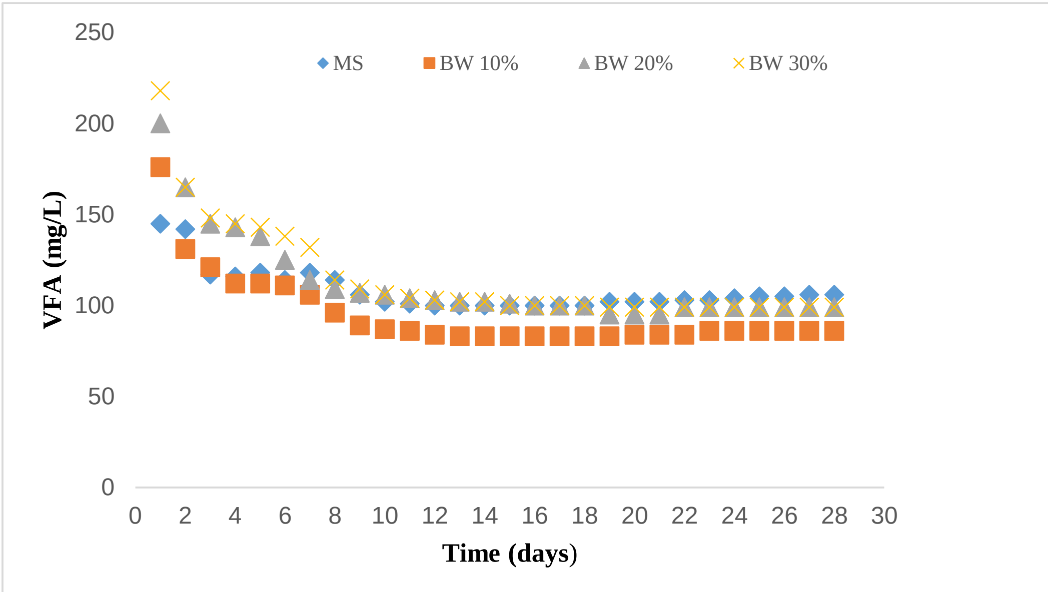


Figure 23. The variation of VFA with time (0%, 10%, 20% and 30% BW)

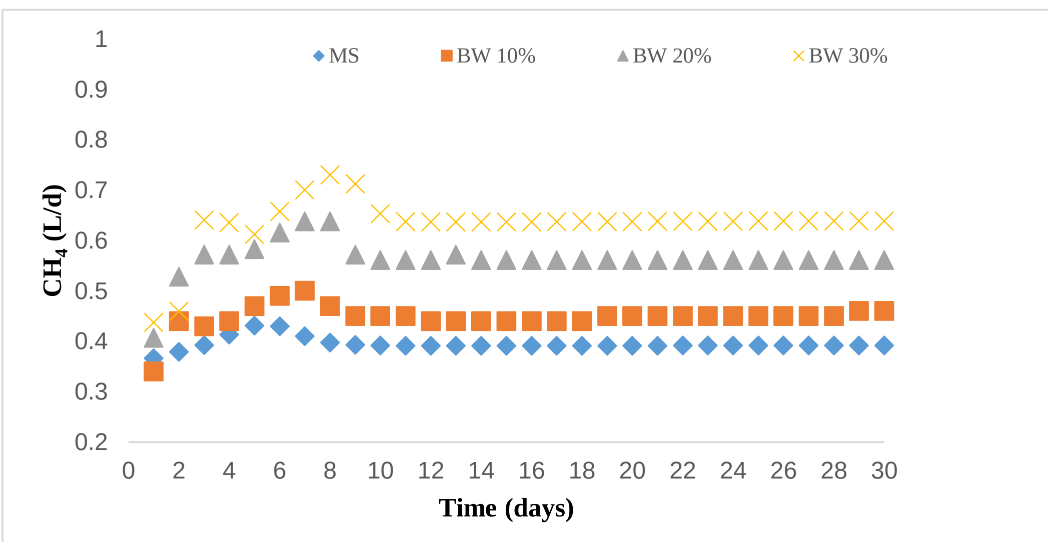


Figure 24. The variation of CH_4 with time (0%, 10%, 20% and 30% BW)

Figure 22 shows the variation in the pH with sludge only and the sludge with different ratios of BW (10%, 20%, and 30%). Injecting BW led to a slight drop in the pH during the first 8 days, particularly with the higher loads of BW (20%, 30%), then no significant fluctuations in the pH values were observed for the rest of the experiment days, which indicates a healthy environment for the anaerobic microorganisms inside the digester. The natural buffer of the system is important for maintaining the pH close to neutral even when a drop occurs.

MS provides the required buffer since BW alkalinity is very low (Table 7, BW alkalinity as CaCO3 = 45 ± 6.4 mg/L). The natural buffer occurs due to the process of proteins degradation which provides the system with ammonia (NH3). The ammonia, reacts with the excess of hydrogen protons to keep the pH values neutral as illustrated by Equation 3 (Metcalf et al. 2013).

$$NH_3 + H^+ \rightarrow NH_4{}^+ \quad (3)$$

In this study, it was found that the pH values were neutral with the different BW loads (Figure 22). No external buffer (lime or soda ash) was required to maintain the pH of the system, which makes the overall economic cost-effectiveness of the process favorable.

The variation of VFA with the increase of BW loads from 10%–30% was illustrated in Figure 16. VFA concentrations increased (176 -218 mg/L) due to the impact of BW especially during the first 10 days. The concentration of the VFA dropped down to an average of 100 mg/L for the rest of the days (Figure 23).

The advantage of adding BW is further revealed in Figure 24. An increase in methane gas production from the digester was noticeable with increased percentage of BW as predicted by the modified model. The average daily production of methane gas was 0.39 L/d when MS was used; methane production was increased to an average of 0.64 L/d when 30% BW was used, confirming the enhancement of the methane production by approximately 60% compared to MS.

Stage 5: Adding BW to MS

[35%, 36%, 37%, 40%, 42% and 44% BW]: [65%, 64%, 63%, 60%, 58%, and 56% MS]
Using the modified parameters in Table 8 in order to determine the imbalance point of the digester, the ADM1 model was run with the ratios 35%, 36%, 37%, and 40% of BW with MS based on COD. The imbalance point based on the model results was reached with the ratio of 37% BW: 63% MS respectively. Figures 25–27 show the failure points as predicted by the model.

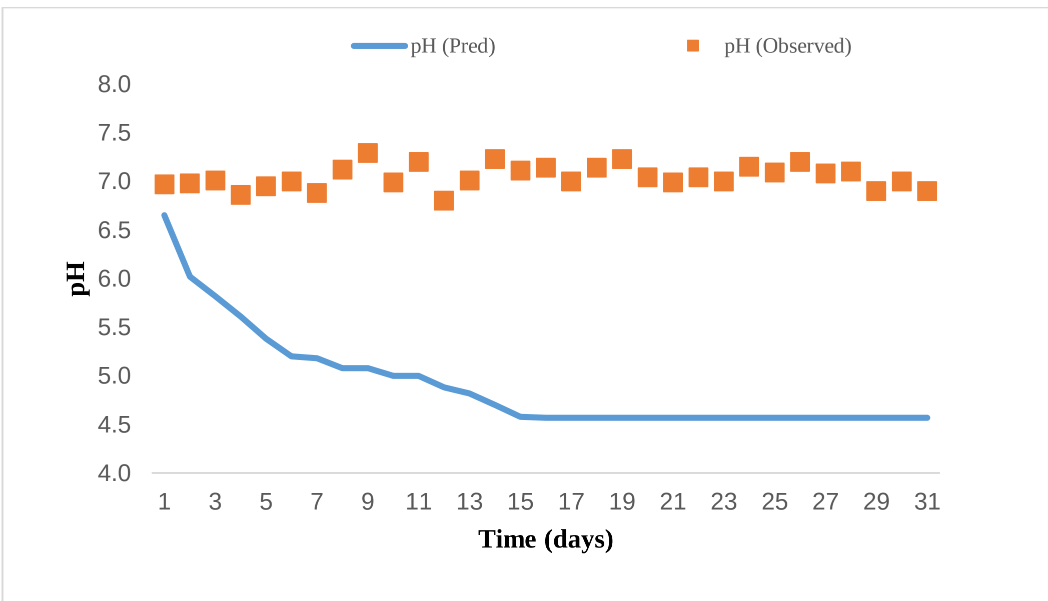


Figure 25. Comparison between predicted and observed pH- 37% BW

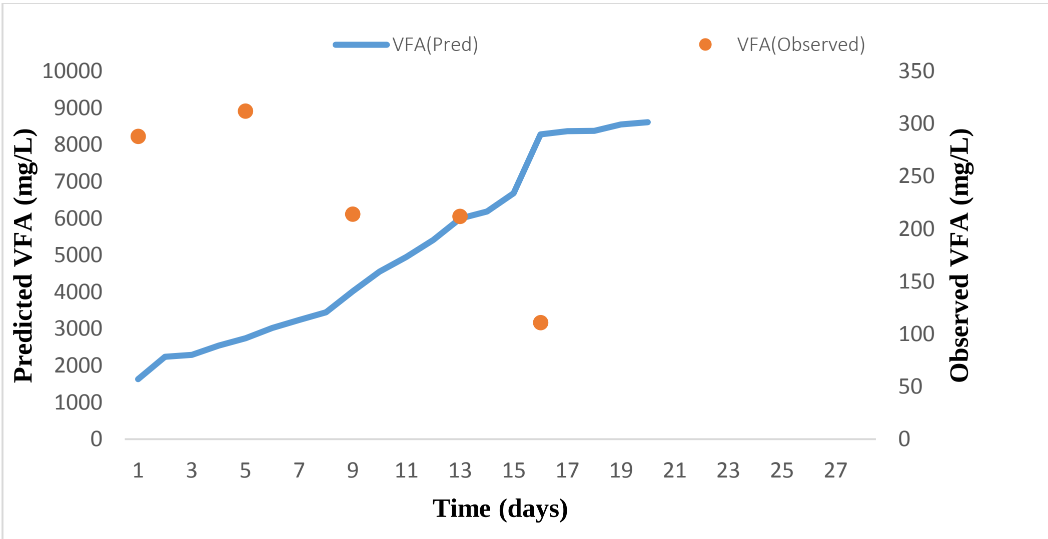


Figure 26. Comparison between predicted and observed VFA- 37% BW

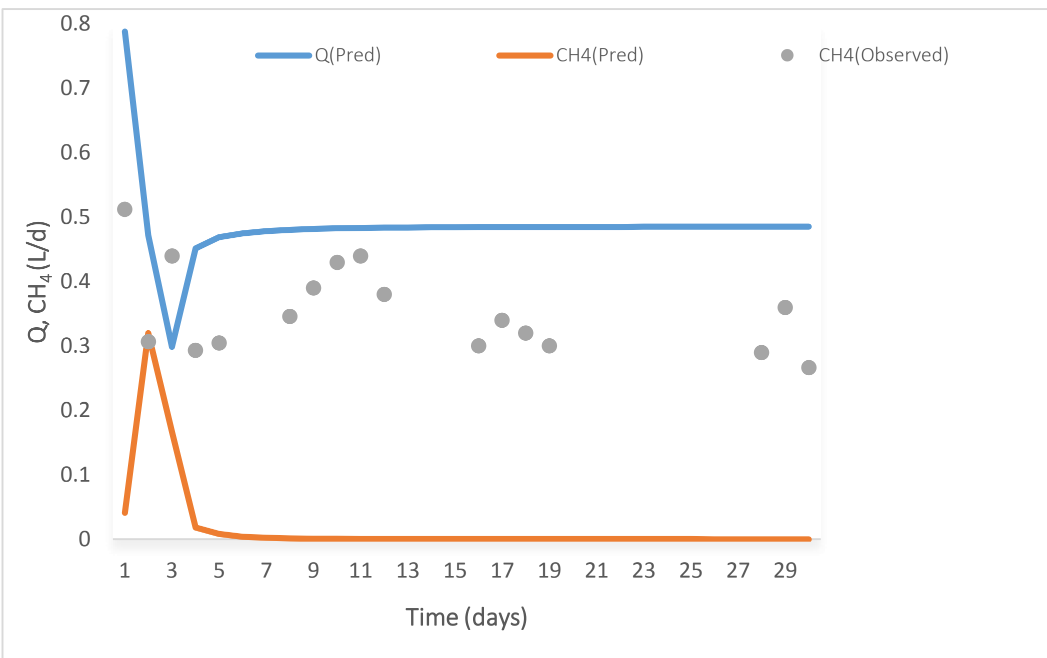


Figure 27. Comparison between predicted and observed Q, CH_4- 37% BW

Based on the model results, the BW would drop the pH to 4.57, VFA would reach 8618 mg/L, and 0% methane gas would be produced. However, with this ratio (37% BW:

63% MS) in the batch reactors, the pH values were still close enough to neutral. Moreover, the measured VFA and methane gas produced indicated no failure detection at this ratio of BW to sludge (37%: 63%) in the batch reactor scale.

In order to reduce the uncertainty associated with the co-digestion of BW and to determine the failure point of the digester, the batch reactors were run again with 40%, 42%, and 44% BW. The results of the batch reactors showed a huge drop in the pH and methane gas with the mixing ratio of 40% BW: 60% MS respectively.

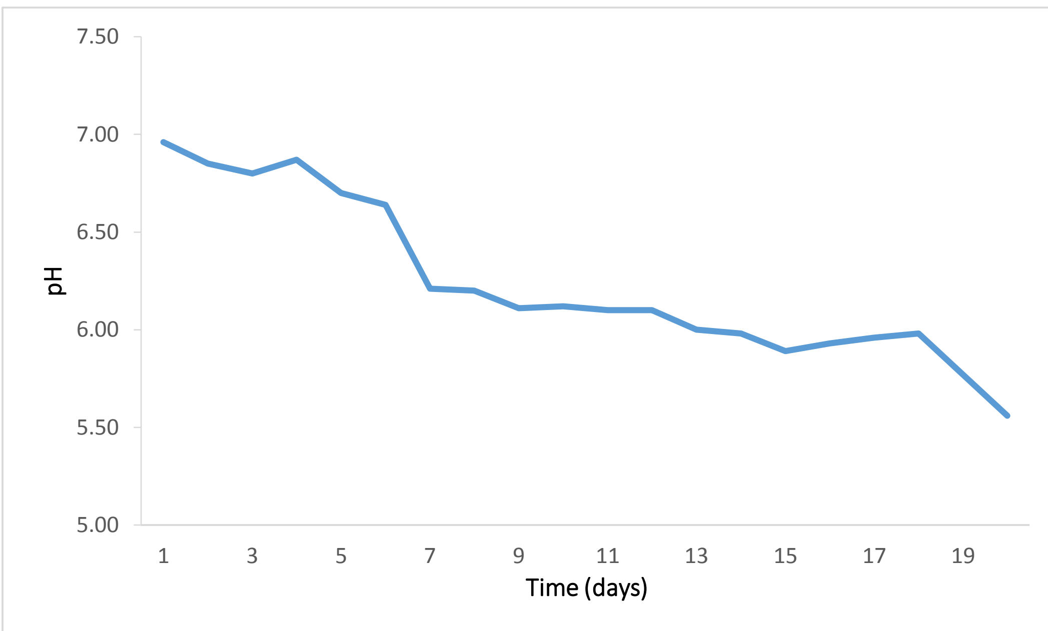


Figure 28. *pH* variation *with time*

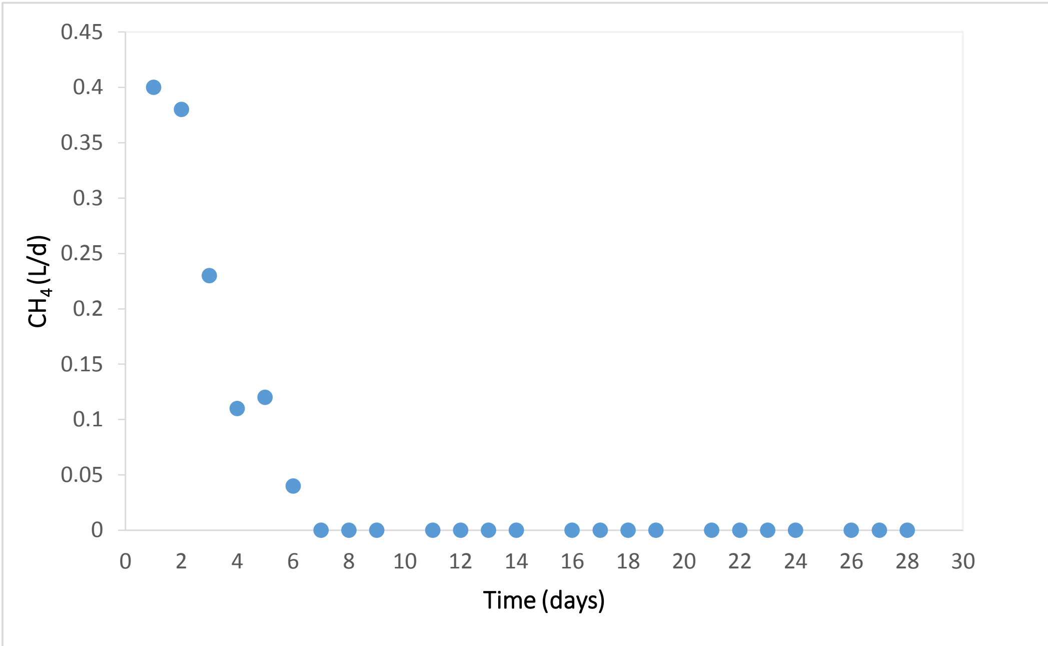


Figure 30. CH_4 variation with time- 40% BW

Based on batch reactor results, the imbalance point was reached at 40% BW. There was a drop in the pH to 5.56 after 20 days of the experiment, and methane gas was not detectable after 7 days.

The results of this study demonstrated that BW is an attractive material that can enhance the production of methane gas when mixed with MS. Although caution must be taken to avoid adding too much BW to MS in order to avoid reactor failure. It was found that the digester is capable of maintaining stability until the maximum range of 37–40% BW to 63%-60% MS ratios (based on COD). Both results (model and experimental) reduced the uncertainty and the risk associated with BW to MS co-digestion.

It is important to use batch scale reactor experiments to determine the stability and the impact of adding BW because BW may contain material toxic to the microorganism community in the reactor, which may not be detected by the ADM1 model. BW also contains a significant amount of metals, which may have negative impact on the microorganisms when co-mixed with MS and this too cannot be detected by the model.

Elements like Na^{+} at high concentrations may inhibit the microorganisms (Hierholtzer and Akunna 2012), while Cl^{-} and SO_4^{-2} may form various inhibitors when they interact with other metals inside the digester (Ye Chen 2007); the modified ADM1 model is unable to detect such inhibitors if found.

The increase in the VFA concentrations was the main reason for the digester failure. Increasing the loads of BW mixed with MS leads to an increase in the VFA, which drops the pH. Another reason that may have contributed to digester failure when 37%-40% BW was added was the C: N ratio. The C: N ratio for optimum digestion and optimal gas production should be in the range of 25- 30:1 C: N respectively. The main source of the N in the co-digestion of BW with MS is the proteins content of the MS. Since BW doesn't include proteins (Table 7, TKN and NH_3 were below the detection limit), the only source of N was the MS.

Based on the results of this study, BW mixed with MS has less nitrogen content and that has less effect on the digester stability due to ammonia (low proteins in the BW). Thus, BW can be considered an advantage co-mixed with MS compared to food waste.

BW contains about 20% lipids which is less than most food waste (30% approximately). Lipids degrade to long chain fatty acids by bacterial activities, and high concentrations of long chain fatty acids are inhibitory to anaerobic microorganisms (Tritt 1992). Lipid-rich material like food wastes from restaurants is not appropriate for municipal digesters since it can readily accumulate inside the digester walls, forming hardened deposit material and reducing the digester volume capacity (He et al. 2011). BW, on the other hand, are not sufficiently lipid - or proteins-rich to cause this problem.

Furthermore, keeping BW from disposing and utilizing them in the way discussed in this research, as good substrate for co-digestion is also beneficial because it is highly rich in organic matter, easily biodegradable, and can be easily pumped (as slurry material). The BW creates good balance with the MS, avoiding most of the inhibitors and toxicants and leads to a high methane production and acceptable process co-digestion stability when mixed within proper ratio limits.

6. Conclusion

The modified ADM1 is a strong tool for predicting and simulating the performance of the anaerobic digester when treating mixed substrate (MS with BW). Modification and validation were applied to the model in order to accurately predict the impact of adding the BW to MS. The modification of the kinetic coefficients of the model improved the ADM1 to become more appropriate for the prediction of the mixed substrate (MS + BW).

Stable performance of the digester was confirmed with 10%, 20%, and 30% of BW addition to MS. The pH, VFA, and propionic acid from observed and predicted results were in the recommended range which reflect a healthy environment for the microorganisms in the digester. An increase in methane gas production (up to 60%) was observed as a result of adding BW.

The imbalanced range of the digester occurred between 37% - 40% BW to MS ratios, based on observed and predicted results of the modified model, and no inhibition was detected before that range.

This research developed an existing mathematical model (ADM1) for addressing the addition of a specific substrate (BW) to MS, in order to reduce the risk and the uncertainty of the digester's malfunction where this substrate actually employed on a large scale.

7. Recommendations

(1) Reclamation of BW will play an important role in its management, it is rich in organic matter and can be applied to produce energy instead of disposals, which will be an environmental benefit to the public.

(2) Further improvement for the ADM1 model is required, to more accurately predict the biogas and hydrogen gas production during the process. Modeling accurately the hydrogen gas is important because hydrogen has a negative impact on the acidogenesis bacteria, and it results in an early stress of the system.

8. Acknowledgments

I would like to thank the Utah Water Research Laboratory for their financial support. Dr. Darwin Sorensen and Dr. David K. Stevens from the Utah Water Research Laboratory for their encouragement and help with this research. Central Weber Sewer Improvement District for the permission to use their facility and to present the data, CSM Bakery Products for the permission to collect the data.

Table 7. Municipal sludge (MS) and Bakery Wastes (BW) characteristics; data were collected from CWSID and CSM Bakery Products, Ogden, UT (2014)

Parameters	Unit	Municipal Sludge [a]	Bakery Waste [b]
pH		7.15 ± 0.09	5.66 ± 0.25
TS [c]	%	4.87 ± 0.34	6.69 ± 0.22
VS [d]	% of TS	84 ± 2.3	91 ± 0.65
COD [e]	mg/L	76492 ± 2516	93673 ± 2109
Alkalinity ($CaCO_3$)	mg/L	4113 ± 229	BDL (<20 mg/L)
TKN [g]	mg/L	1846 ± 98	BDL (< 50 mg/L)
NH_3	mg/L	1123 ± 12	BDL (< 0.8 mg/L)

[a] Municipal sludge samples were collected from CWSID (June- April 2015)

[b] Bakery Waste samples were collected from CSM Bakery Products (December – April 2015)

[c] Total Solids; [d] Volatile Solids; [e] Chemical Oxygen Demand; [f] Biological Oxygen Demand; [g] Total Kjeldahl Nitrogen, [h] Below Detection Limit.

Table 8. Default and modified values for the ADM1 coefficients

Kinetic parameters names	Default values used in the ADM1[a]	Modified Values [b]
Disintegration constant (K,dis)	0.4 (d^{-1})	0.5(d^{-1})
Hydrolysis constant of carbohydrates (Khyd, Ch)	0.25	13(d^{-1})
Hydrolysis constant of proteins (Khyd, Pr)	0.20	10(d^{-1})
Hydrolysis constant of lipids(Khyd, Li)	0.10	10.5(d^{-1})
Dynamic state variable for sugar (xsu,in) [C]	0.00 (Kg COD m^{-3})	0.003(Kg COD m^{-3})
Dynamic state variable for amino acid (xaa,in)	0.01(Kg COD m^{-3})	0.01(Kg COD m^{-3})
Dynamic state variable for fatty acid (xfa,in)	0.01(Kg COD m^{-3})	0.02(Kg COD m^{-3})
Dynamic state variable for acetic acid (xac)	0.01(Kg COD m^{-3})	0.03(Kg COD m^{-3})
Dynamic state variable for propionic acid (xpro,in)	0.01(Kg COD m^{-3})	0.03(Kg COD m^{-3})
Sugar concentration (Ssu)[d]	0.1 (Kg COD m^{-3})	0.3(Kg COD m^{-3})
Dynamic state variable for amino acid (Saa)	0.001(Kg COD m^{-3})	0.001(Kg COD m^{-3})
Dynamic state variable for fatty acid (Sfa,in)	0.001(Kg COD m^{-3})	0.002(Kg COD m^{-3})
Dynamic state variable for acetic acid (Sac,in)	0.001(Kg COD m^{-3})	0.002(Kg COD m^{-3})
Dynamic state variable for propionic acid (Spro,in)	0.001(Kg COD m^{-3})	0.002(Kg COD m^{-3})
Dynamic state variable for butyric acid (Sbu in)	0.001(Kg COD m^{-3})	0.002(Kg COD m^{-3})
Dynamic state variable for valeric acid (Sva in)	0.001(Kg COD m^{-3})	0.002(Kg COD m^{-3})

[a] Values as recommended by (Batstone et al. 2002)

[b] Modified values of the kinetics parameters. [XCh, XPr, and XLi] should be changed each time based on COD of MS:BW

[c] X= Particulate Component S= Soluble Component

Table 9. Statistical analysis results for observed and predicted data

	10% BW			20% BW			30% BW		
	Observed [a]	Pred [b]	P-value [c]	Observed [a]	Pred [b]	P value	Observed [a]	Pred [b]	P value
pH	7.16 ± 0.16	7.22	0.056	7.03 ± 0.07	7.08	0.0761	7.13 ± 0.09	7.15	0.113
VFA[d]	116 ± 9.42	95	0.00788	118 ± 11	117	0.85	118 ± 11.7	116	0.94
Q [e]	0.6 ± 0.02	0.76	0.00098	0.72 ± 0.04	1.00	0.00083	0.90 ± 0.05	1.10	$3.7\text{x}10^{-20}$
CH_4 [f]	0.42 ± 0.03	0.44	0.0058	0.5 ± 0.01	0.52	0.052	0.54 ± 0.057	0.61	0.003

A = average ± standard deviation, b = average, c = calculated probability, d = volatile fatty acids

e = gas flow, f = methane gas

CHAPTER 4

Extending the Applications of the ADM1 to Predict Performance of the Induced Bed Reactor (IBR) Co-Digesting Municipal Sludge with Bakery Waste

Morris Demitry, Conly Hansen, David Stevens and, Michael McFarland.

Abstract

The goal of this research was to examine the stability of the induced bed reactor (IBR) digesting municipal sludge (MS) mixed with bakery waste (BW) by experiment and modeling. It was necessary to modify the ADM1 model to accurately predict the performance of the IBR for this mixed waste. The total mixed influent COD was 50 g/L with hydraulic retention times that varied from 27 to 6 days at mesophilic temperatures. The reactor reached the steady state at each HRT with no sign of inhibition or failure, however, the COD removal efficiency of the digester decreased from 92% to 72% with decreasing HRT. The modified ADM1 outputs agreed well with the measured stability indicators (pH, total volatile fatty acid (TVFA), Q (gas production), percent CH_4) at the longer retention times of 27, and 20 days. The model overestimated the pH, and methane percentage and underestimated the TVFA when the HRT was shorter (12, 9 and 6 days). However, the model predicted well the trends of the observed data and the overall stability process of the digester until 6 d HRT. This research provided an alternative for the disposal of industrial bakery waste and also pointed out the ability of the IBR to manage high waste loads stably, while providing high energy production.

1. Introduction

Treating and reducing industrial waste pollution is a major challenge for engineers and scientists because industrial waste may have a significant negative effect on the environment and treatment of industrial waste is expensive. Treatment of organic industrial waste anaerobically may stabilize the waste and produce biogas as a byproduct of the process. Several studies have demonstrated the benefits of anaerobic treatment of food waste (Bouallagui et al. 2003; Kabouris et al. 2009; Zhang et al. 2007). However, the following operational problems were reported during the anaerobic process: 1) low solubility of the food waste prevented it from being easily biodegradable by the microorganisms, 2) cost of grinding and mixing of the waste so it could be pumped easily to the digester, 3) toxicity and inhibition of the anaerobic microorganisms due to the accumulation of total volatile fatty acids (TVFA) produced when long chain fatty acids, amino acids and monosaccharaides are broken down, 4) toxicity from ammonia nitrogen due to the presence of degradable proteins, and 5) presence of excessive ions such as Mg^{2+}, Ca^{2+}, Na^{+} that can affect the stability of the process (Alves et al. 2001; Angelidaki and Ahring 1992; Angelidaki and Ahring 1993; Bujoczek et al. 2000; Chen et al. 2008; Gavala and Ahring 2002; Kroeker et al. 1979; Lalman and Bagley 2001; McCue et al. 2003; Pereira et al. 2001; Salminen and Rintala 1999; Zeikus 1977).

Generally, municipal wastewater reclamation facilities use anaerobic digestion to stabilize sludge and use the methane produced as a source of energy. The US Environmental Protection Agency (EPA) estimates that more than 181.4 million metric tons of municipal sludge wastes are produced in the United States annually (EPA 2012).

In 2016, the amount of municipal sludge is expected to reach 200 million metric tons with the increase of about 10% in the US population.

A hypothesis of this study is that sewage sludge can be anaerobically co-digested with food waste to produce energy and reduce the amount of the wastes at the same time if carefully operated.

The bakery industry is a major food industry around the world that produces a significant amount of waste daily; bakery waste (BW) is a good candidate to be co-digested with municipal sludge (MS) since it contains high organic matter (carbohydrates and lipids) but minor amounts of protein. There are two kinds of BW The first is waste collected from the pan wash of the bakery industry (cookies, muffins, and pies). The co-digestion of this kind of waste was discussed in detail in our previous studies (Demitry et al. 2015). The second type of BW comes from product residuals or from the process of removing the waste when switching from one product to another.

In this study, the second kind of BW was examined. Digesting the BW alone will likely fail due to its characteristics, having low pH (~4), high concentrations of (TVFA, ~0.45 g/L), and the lack of proteins. However, the co-digestion of BW with other organic wastes containing proteins and alkalinity such as MS will provide the required nutrients and lead to effective anaerobic co-digestion (Neves et al. 2009; Zhang et al. 2011; Zhang et al. 2007).

The Anaerobic Digestion Model Number 1 (ADM1), developed for predicting the dynamic behavior of municipal sludge digestion (Batstone et al. 2002) was used in this study to predict performance of the co- digestion of BW and MS using the Induced Bed Reactor (IBR) anaerobic digester (Dustin 2010; Hansen and Hansen 2005). The input constituents to the model are the chemical oxygen demand (COD) for carbohydrates, proteins, and lipids, the physical characteristics (retention time, liquid and gas volume) for the digester and the temperature. This model has been used extensively for MS systems for predicting process efficiency. The use of the model here will be slightly different than the original intent: to predict the digester's stability indicators (pH, TVFA (mg/L), gas flow rate Q (m3/d), and methane content by volume). The ADM1 models biochemical reactions inside an anaerobic bioreactor and thus can help predict response of the reactor under different operating conditions. However, the model required modification to extend its application to cover co-digestion of MS and BW because the characteristics of the new substrate are different from MS alone. An ADM1 model modified for BW and MS will predict stability indicators that will help with full scale plant design and thus assist in the transfer of this technology from research to practice.

2. Objectives:

The objectives of this research were twofold:

1. Examine the stability of the Induced Bed Reactor (IBR) in the case of anaerobic co-digestion of MS mixed with BW
2. Develop and modify the ADM1 to accurately predict the co-digestion of BW and MS.

3. ADM1 background

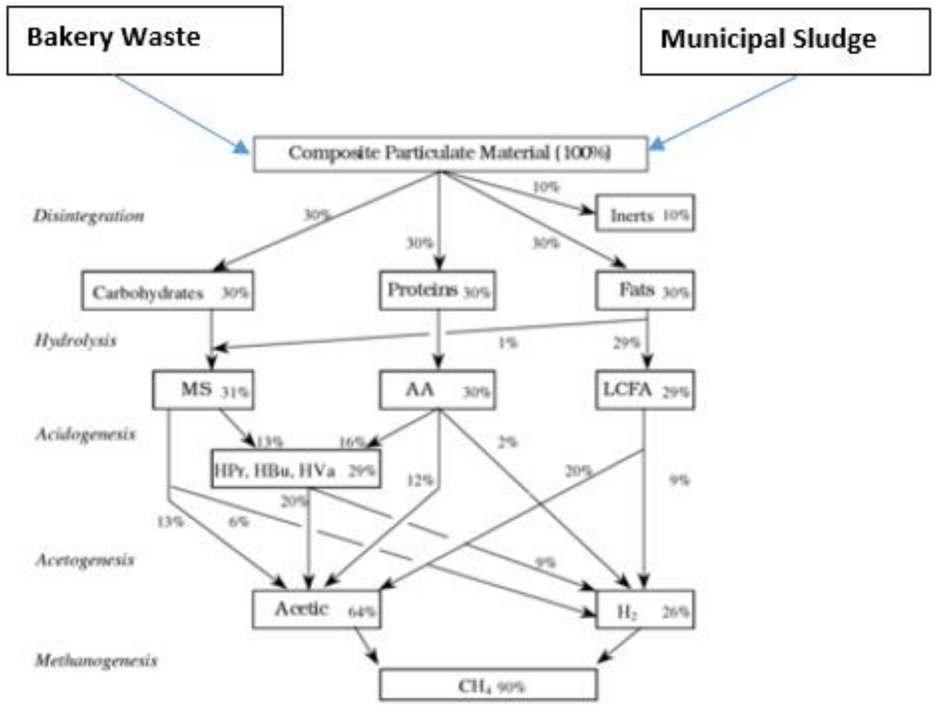


Figure 31. The ADM1 structure (Batstone et al. 2002)

The ADM1 was developed by an IWA group in 2002 (Batstone et al. 2002). The ADM1 is a mathematical structured model that is often used as a framework model that investigators can modify and choose coefficients according to specific substrates and digester configuration. The model consists of a set of 32 differential equations for modeling the rates of change of the different constituents in the liquid and gas phases as follows: 10 for soluble matter degradation, 2 for inorganic carbon and inorganic nitrogen, 4 for particulate matter, 8 for biomass concentrations, 2 for cations and anions and an additional 6 for acid-base reactions (Batstone et al. 2002). The original model includes coefficients and parameters for specific types of organic matter. The model equations are based on a continuous stirred-tank reactor (CSTR) system (Batstone et al. 2002). In order to use the model for different wastes and reactors, modification, optimization, and validation are required (Batstone et al. 2002).

The model simulates the process of anaerobic digestion in four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis as shown in Figure 1. There are two types of methanogenesis, one uses hydrogen gas (H_2) as a substrate, and the other uses acetic acid as shown in Figure 2 (Demirel 2014). One of the original model's assumptions is that the majority of methane produced in an anaerobic digester is by acetoclastic methanogenesis or degradation of acetic acid to methane rather than hydrogenotrophic methanogenesis; production of methane from hydrogen (Batstone et al. 2002). The ratio between the two pathways respectively was assumed in the ADM1 model to be 64:26 based on COD as shown in Figure 1. This statement agrees with previous studies regarding the major role of acetoclastic methanogenesis for the formation of methane in the process of anaerobic digestion of sewage sludge (McCarty 1964; Metcalf et al. 2013; Smith and Mah 1966). While the previous studies demonstrated the role of acetoclastic methanogenesis for methane formation from sewage sludge, Traversi et al, (2011) concluded that methanogen type and diversity is dependent on the feed characteristics and process conditions (Traversi et al. 2011). Based on the conclusion of Traversi et al, in (2011), either kind of methanogenesis (hydrogenotrophic or acetoclastic) may have the major role for methane formation during anaerobic digestion. However, despite the increasing attention on anaerobic digestion of biomass for production of methane, there is relatively little information specifically about the activity and the performance of both acetoclastic methanogenesis and hydrogenotrophic methanogenesis (Demirel and Scherer 2008) in various situations. Differences in the digester's operation and substrates affect the behavior of each group of methanogens. Therefore, the change in the IBR's environment due to adding BW to the system and the changes in the HRT from 27 to 6 days, enhanced the production of biogas through the increase of hydrogenotrophic rather than acetoclastic methanogenesis. This assumption was based on other research that demonstrated the role of hydrogen gas in methane formation and demonstrated that hydrogenotrophic methanogens were the dominant population (Demirel 2014; Demirel and Scherer 2008; Schmidt et al. 2000). Moreover, Padmasiri et al. (2007) reported that the levels of hydrogenotrophic methanogens increased during decreased reactor performance (Padmasiri et al. 2007).Other researchers reported significant impacts of the OLR, HRT and temperature on a decrease of acitoclastic methanogenesis in the system and a dramatic increase in TVFA concentrations (Blume et al. 2010; Krakat et al. 2010; Krakat et al. 2011).

Suggested modification for the ADM1

The modification to the model was made by changing the ratios between acetic acid and hydrogen gas production as shown in equations 3 and 4. These changes were made to reflect the assumption that in the case of MS mixed with BW, more methane was produced through H_2 (hydrogenotrophic methanogenesis) than acetic acid (acetoclastic methanogenesis). However, the changes in the ratios between acetic and hydrogen were made by trial and error until the model predicted the process stability best under different

HRT's. The ratio between H_2:Acetic acid in the modified model is 48%:42%, respectively. The change in the ratio is shown in the following equations:

The original equations in the ADM1 ((Batstone et al. 2002):

$$\frac{dac}{dt} = \tau\left(S_{ac,in} - S_{ac}\right) + ((1 - Y_{su})F_{ac,su}P_5 + (1 - Y_{aa})F_{ac,aa}P_6 + 0.7\left(1 - Y_{fa}\right)P_7 + 0.31(1 - Y_{c4})P_8 + 0.80(1 - Y_{c4})P_9 + 0.57\left(1 - Y_{pr}\right)P_{10} - P_{11} \qquad (4)$$

$$\frac{dh_2}{dt} = \tau\left(Sh_{2,in} - dSh_2\right) + ((1 - Y_{su})F_{h2,su}P_5 + (1 - Y_{aa})Fh_{2,aa}P6 + 0.30\left(1 - Y_{fa}\right)P_7 + 0.15(1 - Y_{C4})P_8 + 0.20(1 - Y_{c4})P_9 + 0.43\left(1 - Y_{pro}\right)P10 - P_{12} - P_t \qquad (5)$$

The modified equations:

$$\frac{dac}{dt} = \tau\left(S_{ac,in} - S_{ac}\right) + \left((1 - Y_{su})F_{ac\_su}P_5 + (1 - Y_{aa})F_{ac\_aa}P_6 + 0.5\left(1 - Y_{fa}\right)P_7 + 0.2(1 - Y_{c4})P_8 + 0.4(1 - Y_{c4})P_9 + 0.50\left(1 - Y_{pro}\right)P_{10} - P_{11}\right) \qquad (6)$$

$$\frac{dh_2}{dt} = \tau\left(Sh_{2,in} - Sh_2\right) + (1 - Y_{su})Fh_{2-su}P_5 + (1 - Y_{aa})Fh_{2-aa}P_6 + 0.5\left(1 - Y_{fa}\right)P_7 + 0.26(1 - Y_{C4})P_8 + 0.6(1\text{-}Y_{C4})P_9 + 0.50\left(1 - Y_{pro}\right)P_{10} - P_{12} - P_t \qquad (7)$$

where S_{ac} = soluble component for acetic acid (kg COD m^{-3}), S_{h2}= soluble component for hydrogen gas (kg COD m^{-3}), Y_{su}= yield of biomass on carbohydrates, Y_{aa}=yield of biomass on amino acids, Y_{fa} =yield of biomass on long chain fatty acids, Y_{su}=yield of biomass on butyric acid, Y_{pro}= yield of biomass on propionic acid, F_{ac_aa}= yield of acetic acid from amino acid, F_{h2_aa}=yield of hydrogen gas from amino acid, P_i= Process i, , □=inverse of residence time, Q/V_{liq} (d^{-1}), Q=flow rate (m^3/d), V_{liq}=liquid volume of the digester (m^3), P_t=transfer rate of hydrogen gas.

In addition, some of the kinetic parameters of the model were changed using trial and error to improve the model prediction to reflect the co-digestion situation of MS and BW as shown in Table 10:

Table 10. Kinetic coefficients for modified ADM1 model

Parameters	Name	Unit	Initial Values	Estimated Values
K dis	Disintegration Constant	Day $^{-1}$	0.4	0.5
K hydr Ch	Carbohydrates hydrolysis constant	Day $^{-1}$	0.25	13
K hyd Pr	Proteins hydrolysis constant	Day $^{-1}$	0.2	10
K hyd Lip	Lipids hydrolysis constant	Day $^{-1}$	0.1	10.5

The initial values were obtained from (Batstone et al. 2002)

The estimated values for Municipal sludge mixed with Bakery Waste

4. Materials and Methods

The stability indicator parameters (pH, TVFA, gas flow, and methane content) were monitored in order to examine the stability of the IBR treating MS and BW. The experimental work was done using a pilot scale IBR developed at Utah State University to apply high-rate anaerobic digestion techniques to high solids content substrate (Hansen and Hansen 2005). The IBR total volume was 60 liters, with liquid volume of 54 liters and gas volume of 6 liters. In this study, the IBR was operated under mesophilic temperature (40°C).

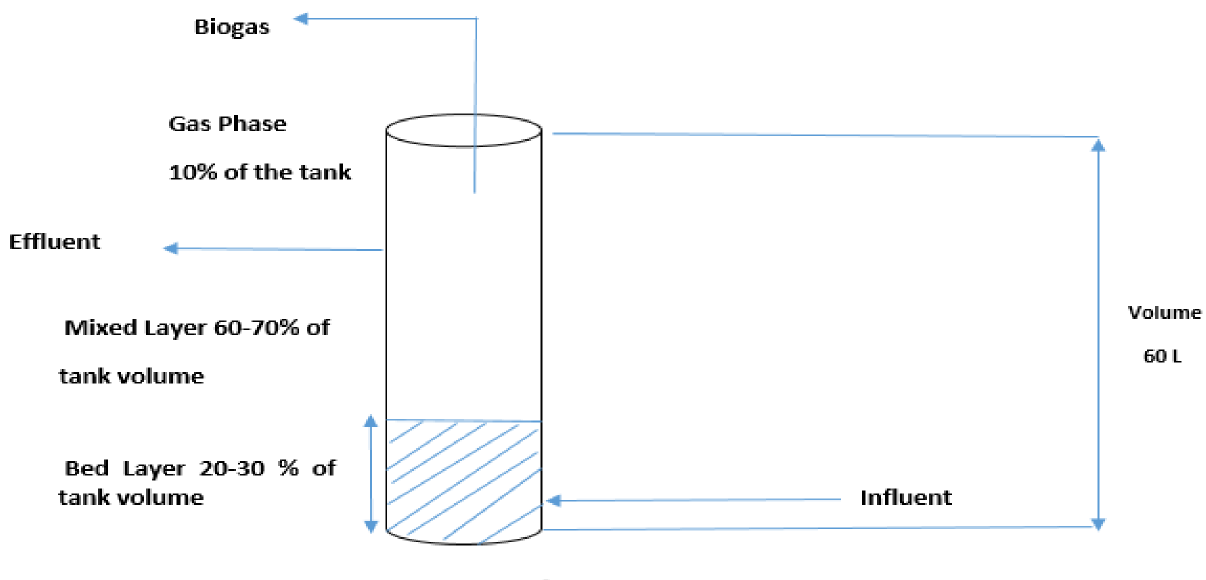


Figure 32. IBR cross-section

The municipal sludge used in the IBR was obtained from Central Weber Sewer Improvement district, Ogden, UT; the BW was obtained from CSM Bakery Products, Ogden, UT. The MS and BW were collected in the period of August, 2015 to February 2016. The BW and MS were mixed based on COD; the ratio was 50:50% MS:BW. The IBR was fed with the mixed solution at various retention times/organic loading rates. The hydraulic retention times (HRT) in this research, were, 27, 20, 18, 12, 9 and 6 days respectively. The mixed solution was fed to the reactor 6 times per day using automated system (Omron industrial automation H3CR-F, Kyoto, Japan).

Samples were collected from the effluent side of the IBR, pH was measured with an Oakton Vernon Hills,(IL USA) meter and TVFA measured using HACH method 8196(HACH 2014). Ammonia nitrogen was measured using HACH method 10031(HACH 2015). The lab temperature was 24°C; the biogas was collected and the volume was measured using Tedlar gas bags (CEL scientific corporation, Cerritos, CA, USA). The volume of the measured gas at the Food Engineering Laboratory was corrected to an equivalent volume of 1 atm pressure using equation 8:

$$P_1V_1 = P_2V_2 \quad \text{..} (8)$$

Where:

P_1 = The average atmospheric pressure at the lab (0.86 atm)

V_1 = The measured volume of the gas(m^3)

P_2 = The atmospheric pressure (1.0 atm)

V_2 = Corrected gas volume (m^3)

The correction was done because the ADM1 assumed the atmospheric pressure is 1 atm, while the average atmospheric pressure at Logan, UT, USA is 0.86 atm.

Methane and carbon dioxide content of the gas were measured using an Agilent 6890 GC, RT-M sieve 5A Plot capillary column (Restek) (Agilent, Santa Clara, CA).

Digester influent TCOD of the mixed and diluted (tap water) waste was 50 ± 1.17 g/L; the ratio between the BW:MS was 50:50 based on COD. The IBR was operated at mesophilic temperature (40 °C).

All the above mentioned parameters were measured in duplicate or triplicate and quality control protocols were applied for the analytical instruments calibrations. Data were recorded in spreadsheets and R database structures for analysis. Table 11 shows characteristics of the MS and BW.

Table 11. Municipal sludge and bakery waste characteristics

Parameter	Units	Municipal Sludge (MS)	Bakery Waste (BW)
pH		**6.98 ± 0.21**	**4.00 ± 0.28**
TS	**%**	**5.15 ± 0.34**	**9.35 ± 0.22**
VS	**% of TS**	**91 ± 2.3**	**96 ± 0.65**
COD	**g/L**	**76 ± 8.16**	**175 ± 13.64**
Alkalinity ($CaCO_3$)	**mg/L**	**4150 ±156**	**BDL(<20mg/L)**
TKN	**mg/L**	**2118 ± 89**	**BDL(<50 mg/L)**
NH_3	**mg/L**	**1100 ± 104**	**BDL(<0.8mg/L)**

Each point is the average of triplicates. ± shows standard deviations among replicates.
BDL= Below Detection Limits.

The IBR stability and performance were evaluated with organic loading rates ranging from relatively low (~1.9 kg COD m^{-3} d^{-1}) at a 27 d HRT to high (~8.5 kg COD m^{-3} d^{-1}) at a 6 d HRT. The work in this study was done using the six different retention times shown in Table 12.

The decision to switch from one HRT to another was based on whether the IBR performance reached stable steady-state situations, assumed to be occurring when digesters were operating at or near their recommended levels for the stability indicators (pH ~7, TVFA <2000 mg/L, NH_3 <1500 mg/L) and when gas production and gas rates were relatively constant (±10% per day)) (Kroeker et al. 1979).

Table 12. Experimental phases, daily digester feed, the HRT, the OLR, and the rate of methane produced per COD converted

Phase	Feed Q (L/d)	Retention Time (HRT, d)	OLR (Kg COD $m^{-3}d^{-1}$)	Rate of methane production ($\frac{L\,CH_4}{g\,COD}$)
1	**2**	**27**	**1.85**	**0.42**
2	**2.7**	**20**	**2.48**	**0.44**
3	**3**	**18**	**2.78**	**0.42**
4	**4.5**	**12**	**4.15**	**0.42**
5	**6**	**9**	**5.56**	**0.42**
6	**9**	**6**	**8.33**	**0.35**

ADM1 Model

The ADM1 equations in this study were coded and implemented using R programming software for statistical computing (Team 2015). R was chosen among several options because of its statistical and graphics capability. The differential equations were coded as R functions and integrated using the LSODE method from the deSolve library (Soetaert et al. 2010).

5. Results and Discussion:

The original ADM1 model was used to simulate performance at the longer HRTs and was unable to predict the stability indicators (pH, TVFA (mg/L), Q (m3/d), and CH4 %) and overall stability for MS mixed with BW (COD=50 g/L; different HRT's, and temperature = 40°C). The original model did not include the necessary kinetic coefficients (Table 10) required to predict stability parameters for the case of co-digestion of MS and BW.

Accordingly, modifications to the ADM1 model were required in order to extend the ADM1 application to the case of the mixed waste in this study.

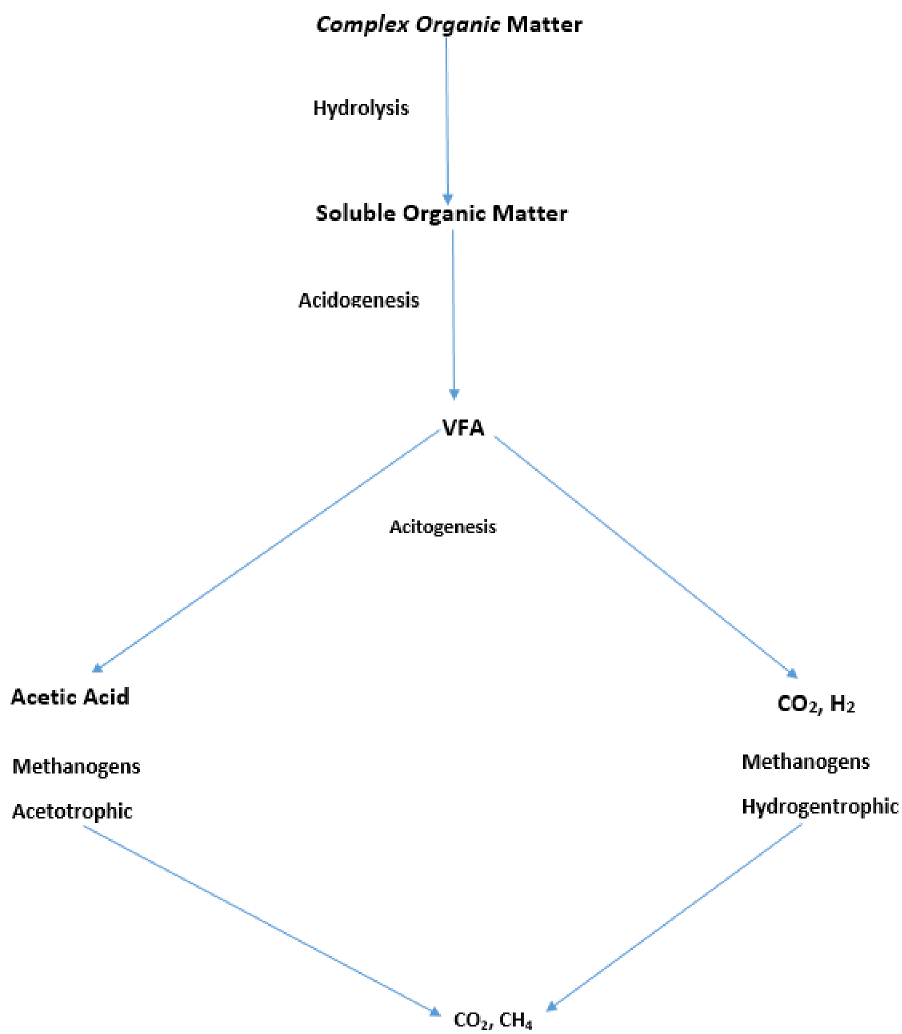
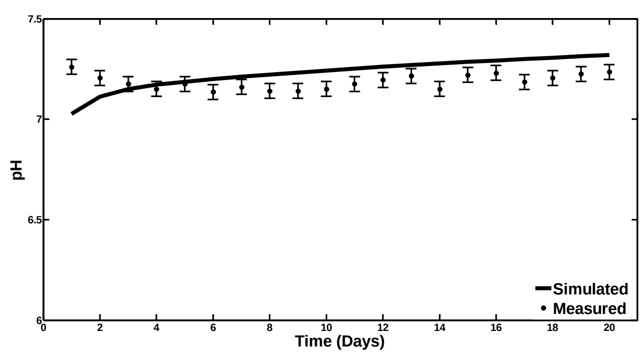


Figure 33. The stage of anaerobic digestion process adapted from (Demirel 2014)

The ADM1 was modified based on recent studies reporting hydrogenotrophic methanogenesis for methane production favored over acetoclastic methanogenesis as described by Equations 4-7.

Figures 4 -7 show the results for phases 1, 2, 4, and 6 respectively of the experiment using the modified model, in which each observation represents the average of duplicate samples.

Results for phase 1 (HRT = 27 days) are shown in Figure 33. The modified model outputs agree well with the observations in case of pH, TVFA (mg/L) and gas flow (m^3/d), while acceptably in predicting the measured methane percentage (the difference between simulated and measured =±10 %). Moreover, the model outputs and the observations have the same trends (from days 2-20). The fluctuations in the measured stability indicators during the process were very small. Relatively high methane percentage (70.65 ± 1.45%) was observed at a COD removal efficiency of 92 ± 0.67%. The effluent NH_3 = 345 ± 14.2 mg/L, and TVFA concentration remained below 100 mg/L, all signs of stable operation.



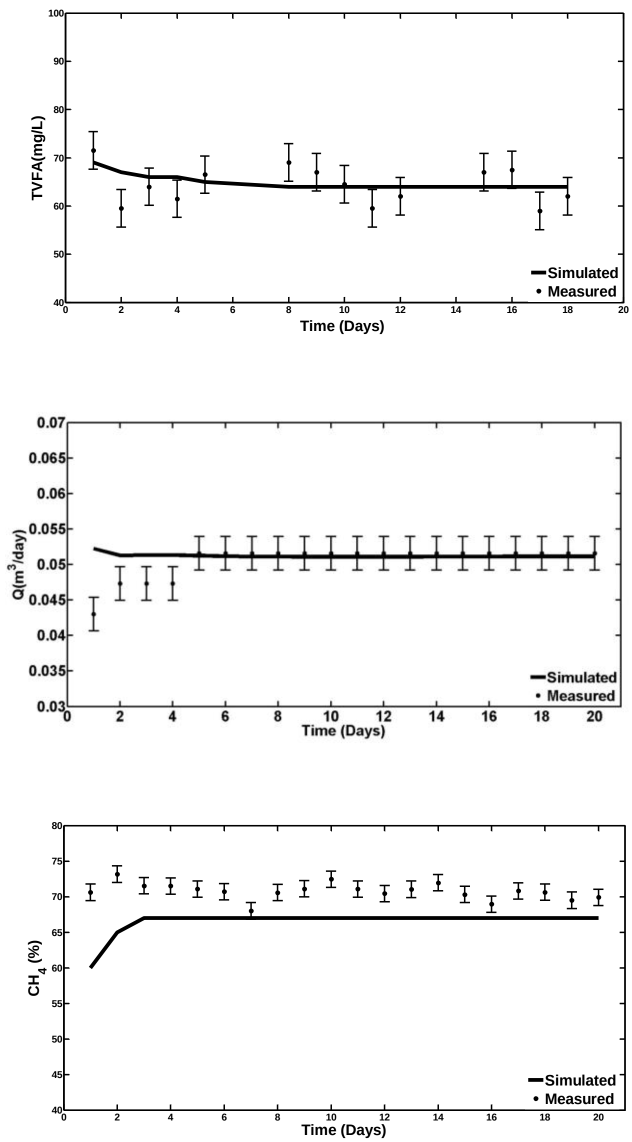
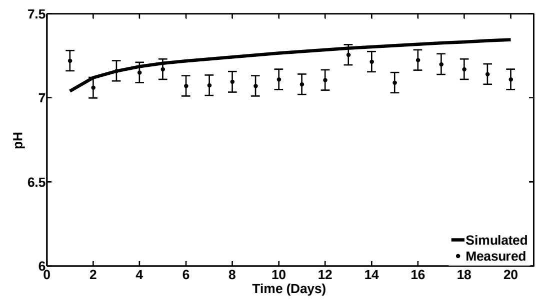
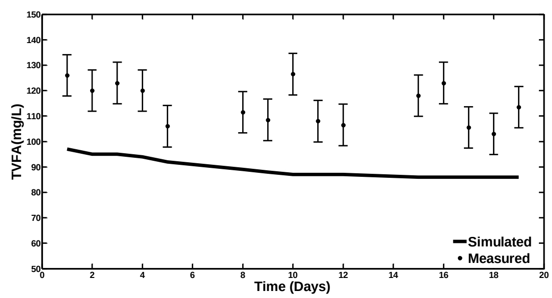
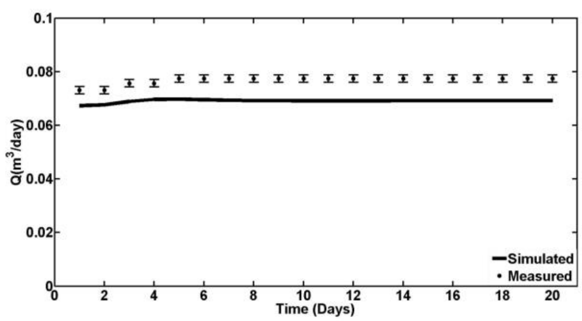


Figure 34. Comparison between simulated and measured data, a=pH, b=TVFA (mg/L),c=Q(m^3/d) and d=CH_4 %, the error bars represents the standard deviation phase 1

In this Phase the IBR was under stable steady state conditions since the reactor was operating at or near the recommended levels for effective digesters, pH= 7.5-6.5, TVFA ≤ 2000 mg/L, propionic acid ≤ 900 mg/L, ammonia NH_3 ≤ 1500 mg/L (Bitton 2005; McCarty 1964; Metcalf et al. 2013; Wang et al. 2009), and there was stable biogas production and CH_4 percentage (±10 % per day). However a high methane percentage content in the biogas, in the range of 65 - 75%, reflects a healthy digester (Kroeker et al. 1979; Turovskiy and Mathai 2006). The rate of methane production per COD removed was 0.42 L CH_4/g COD during phase 1







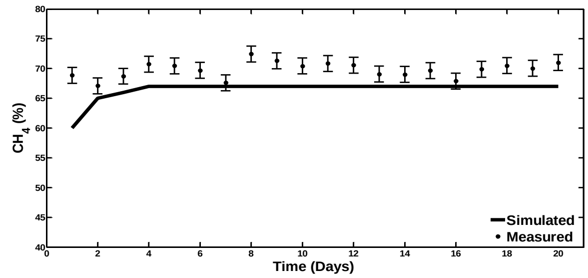
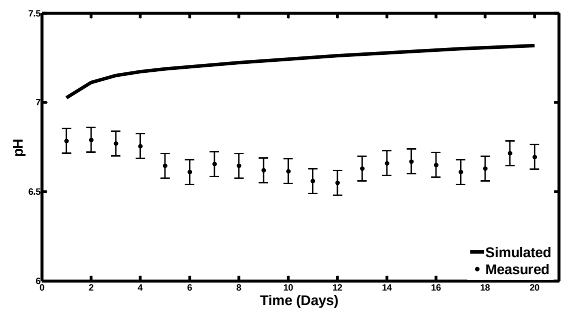
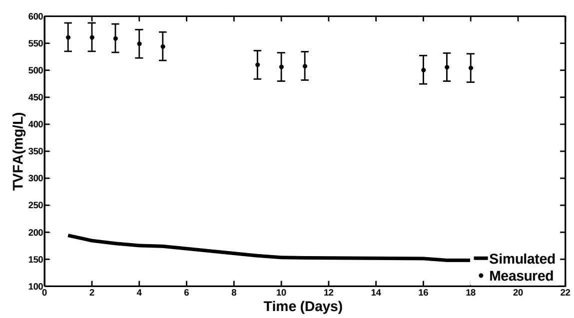


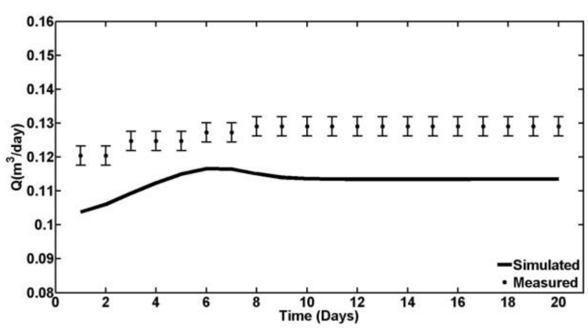
Figure 35. Comparison between simulated and measured data, a=pH, b=TVFA (mg/L), c=Q(m^3/d), d=CH_4%= the error bars represents the standard deviation- Phase 2

Results for phase 2 (HRT= 20 days) are shown in Figures 34. The modified model reasonably predicted the pH, gas flow (m^3/d) and methane percentage (%), while underestimating the TVFA (mg/L). The simulation and the observations have the same trends (Day 4- day 20) as shown in Figure 34. There were no fluctuations in the observations: the IBR was run under steady- state and effective performance conditions. The COD removal was 90 ± 1.4 % and the average effluent NH_3 was 358 ± 17.8 mg/L, similar to Phase 1. The increase in the OLR from 1.85 Kg COD M^3 d^{-1} in Phase 1 to 2.48 Kg COD M^3 d^{-1} in Phase 2 did not affect the digester performance, both the model outputs and the observations show effective digester performance and no inhibition or stress was detected in Phase 2. The rate of methane production per COD removed was 0.44 L CH_4/g COD during phase 2, which was slightly higher than phase 1 (0.42 L CH_4/g COD).

In phase 3 (HRT= 18 days), the digester performance was stable, the pH values were close to phase 2. Slightly increase in the TVFA (mg/L) accumulation and in the gas production (m3/d) were noticed compared to phase 2. Despite the increase in the TVFA, there were no inhibition or stress detected during phase 3. Because the IBR was under steady state conditions, the decision was taken to increase the OLR to reach 4.15 kg COD m-3d-1 as shown in phase 4. The rate of methane production per COD removed was 0.42 L CH4/g COD during phase 3, which demonstrated the stable and effective performance of the IBR since the rate of methane production was stable during phase 1- 3.







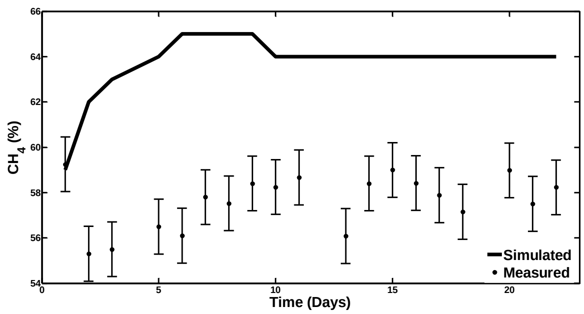


Figure 36. Comparison between simulated and measured data, a=pH, b=TVFA (mg/L, Q= (m^3/d), d=CH_4%, the error bars represents the standard deviation phase 4

In Phase 4 (HRT=12 days), the digester performance went down when the OLR was increased to 4.15 kg COD m^3 d^{-1}. A dramatic increase in the observed TVFA was seen, along with the drop in the observed pH (6.7-6.9). However, despite the increase in the measured TVFA and the drop in pH values, stable performance was achieved and the digester produced significant amounts of biogas (0.15 M^3/d) and a stable percentage of CH_4 (59%) at this shorter HRT. This demonstrated the stability of the process in Phase 4 since process instability is usually indicated by rapid increases in the TVFA and decrease in the methane production (Kroeker et al. 1979). Moreover, stable methane production per COD removed from the IBR was noticed (0.42 L CH_4/g COD) as shown in Table 12.

In Phase 4 the model outputs did not agree with the observations as shown in Figure 35. The model overestimated the pH, underestimated the TVFA (mg/L), while it reasonably predicted the gas flow (m^3/d) from the IBR and overestimated the methane percentage. Even though the model did not predict the stability indicators in Phase 4, it was still able to predict the digester's trends and the overall process stability reflecting an active digester performance.

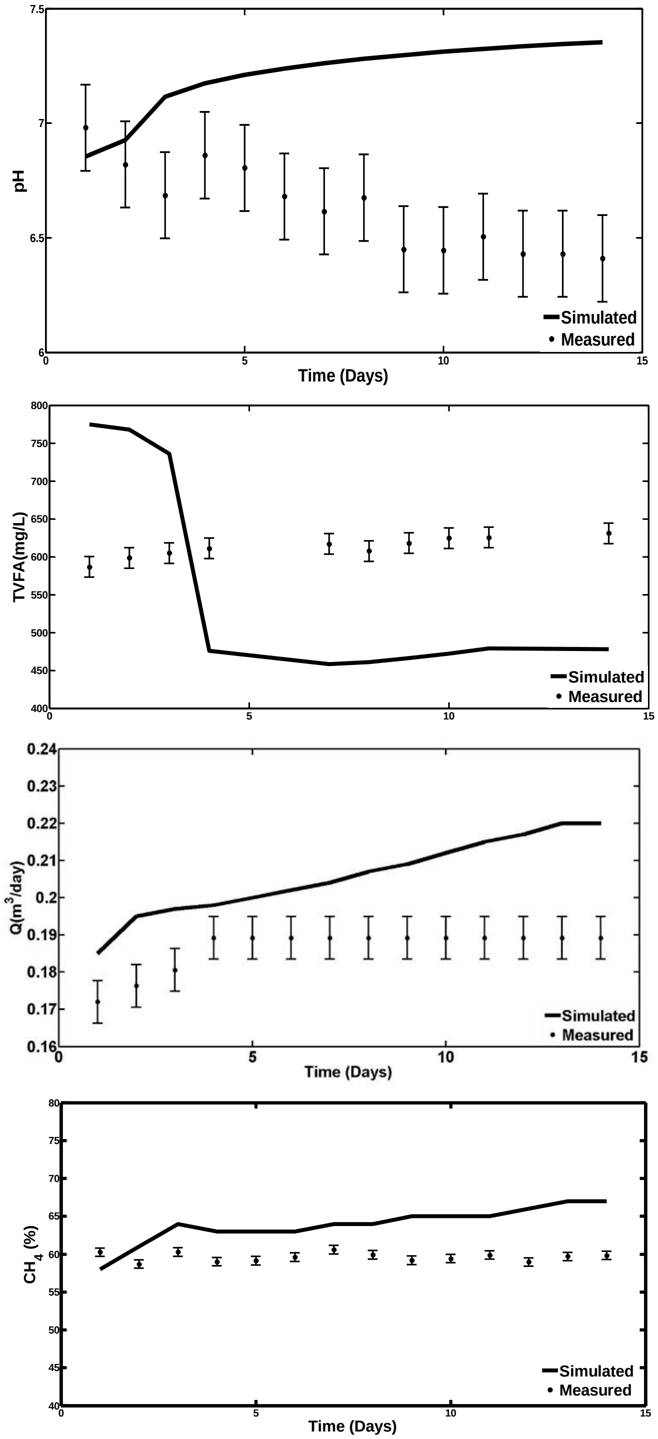


Figure 37. Comparison between simulated and measured values, a=pH, b=TVFA (mg/L, Q= (m^3/d), d=CH_4%, the error bars represents the standard deviation phase 6

In Phase 6, at an HRT of 6 days (Figure 36), the digester was still effective and stable. The observations show an increase in TVFA to ~611 mg/L compared to previous phases, and a drop in the measured pH values (to ~6.7), but at the same time shows an increase in the gas production (~0.19 m^3/day). Stability parameters indicated a stable steady state of the IBR in Phase 6. However, a decrease in the rate of methane production from the IBR per COD removed was noticed in Phase 6 (0.35 L CH_4/g COD). The reduction of the methane production rate in Phase 6 may be an indicator of a partial stress in the system.

On the other hand, the model overestimated the pH (by +12%), while underestimated the TVFA (by 20%). The model predicts acceptably (+10%) the gas flow (m3/d) and methane percentage (%) in the first 10 days, and overestimated them in day 11 - day 15 as shown in Figure 36. However, the model successfully predicted the general trend of the IBR and the stability situation in Phase 6. At any rate, the differential equations of the model are non-linear and it is complicated to optimize all the model's coefficient to predict well the process of the anaerobic digestion. Several studies have reported disagreement between the model and the observed data for continuous and semi continuous stirred reactors ((Fezzani and Cheikh 2008; Parker 2005; Razaviarani and Buchanan 2015; Shang et al. 2005).

In this study, the main reason for the disagreement between the model outputs (simulated) and the observed data from the IBR in low HRT (≤12 days) is because the ADM1 model considered that the digester is a single stirred tank reactor (Batstone et al. 2002) not an IBR, which behaves more like 2 tank reactors in series (Figure 31), with the first having a high biomass concentration and the second a low biomass concentration. Accordingly, the ADM1 needs more modifications to predict the IBR performance especially when the HRT ≤12 days by considering mass balances separately for the two different reactors.

These results demonstrated the effective performance of the IBR and its ability for handling high OLR (8.33 kg COD m-3d-1) of mixed organic matter. This stable performance at low HRT is characteristic of the IBR since the bed of the reactor retains the microbes in the bottom 20-30% of the tank (Figure 31), and helps to prevent the system from being stressed until the digester adapts to the substrate leading to reactor stability (Dustin 2010; Hansen and Hansen 2005).

The co-digestion of MS mixed with BW is cost-effective for energy recovery. There was a considerable increase in the biogas and methane percentage in the presence of bakery waste. No chemical buffer (NaOH or Na2CO3) was required during the process to buffer the pH as the MS provided adequate buffering for the system to keep the pH in the recommended ranges (6.5-7.5). Also, the BW characteristics avoided most of the problems related to the digestion of food waste as mentioned in the literature since the BW doesn't required any grinding like more typical food waste from restaurants, fruits waste and core waste, moreover, the BW is highly soluble when mixed with MS which helps the microorganisms to utilize it quickly.

The digester was stable during all the phases but the efficiency of the IBR removing organic matter was affected as the loading rate increased and the residence time decreased (Figure 37). In Phase 1 (HRT = 27 days, OLR = 1.85 kg COD m-3d-1) the IBR successfully removed 92% (as COD) of the initial organic matter and the methane was relatively high (72%). In Phase 4 (HRT = 12 days, OLR = 4.15 kg CODm-3d-1) the efficiency decreased to reach 82% and CH4 content dropped to 58% while in Phase 6 (HRT = 6 days, OLR = 8.33 Kg COD m-3d-1) the organic matter removal efficiency dropped to 72% and the CH4 was still at the range of 58% of the biogas (Figure 37).

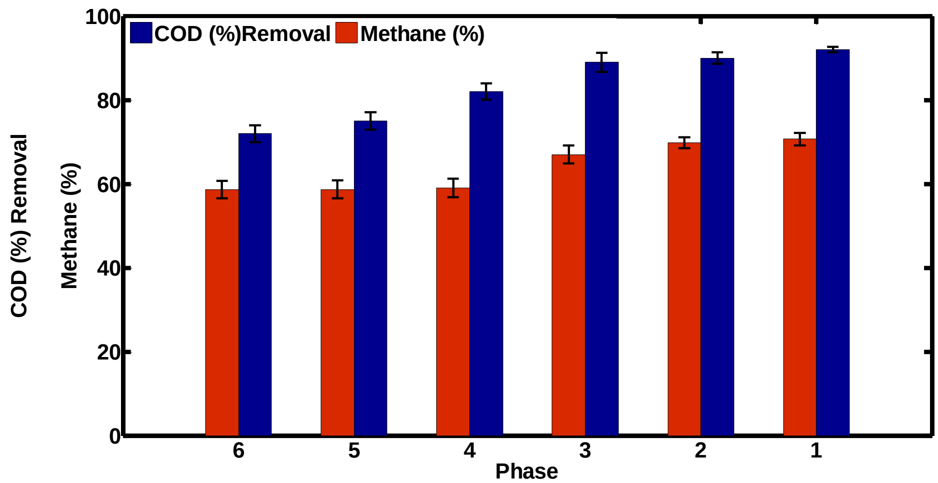


Figure 38. The relation between steady state % removal of COD, percentage methane content and HRT- IBR

6. Conclusion

The Induced Bed Reactor (IBR) was evaluated for co-digesting municipal sludge (MS) and bakery waste (BW) at a 50%:50% ratio of MS: BW based on COD. Highly stable performance for the IBR was achieved over a broad range of retention times of (27, 20, 18, 12, 9 and 6 days). The IBR remained stable at all HRTs though the TVFA did increase significantly when the HRT dropped below 10 days. Stable methane production per COD removed (0.42 L CH_4/g COD) was reported in Phase 1 through Phase 5, while a reduction of methane production rate (0.35 L CH_4/g COD) was noticed in Phase 6. All these results confirm that BW and MS provide the nutrient balance for the IBR's microorganisms. Also, these results pointed out the ability of the IBR to handle high COD loading with relatively short HRT for this mixed substrate.

The ADM1 model was modified to more accurately predict the co-digestion of BW and MS by IBR. The modification increased the model's ability to predict the stability indicators of the digester in all phases. The modified model was accurate and agreed reasonably well with the measured stability indicators (pH, TVFA (mg/L), Q (m^3/d) and methane content by volume (%)) especially with 27, 20 and 18 HRT. The modified model couldn't predict accurately the stability parameters with shorter HRT since the IBR acts as two different reactors (bed and mixed reactors).

This research shows potential for anaerobic digestion of bakery waste management and its role for energy recovery for treatment plants. It also demonstrated the benefits of the modified ADM1 model as a useful tool to support decision making for anaerobic digestion of BW and MS.

7. Acknowledgment

I would like to thank the Utah Water Research Laboratory for financial support, also Dr. Darwin Sorensen and Dr. Shaun Dustin for their effort and support.

I would like also to thank Dr. Jianming Zhong for his effort regarding the preparation of the food engineering lab and the set-up of the induced bed reactors to be ready for the experiment.

CHAPTER 5

Research Conclusion

The Stability index developed based on the rate of methane gas produced per destroyed volatile solids was found to be (0.4L CH_4/g ΔVS). It has the ability to predict the failure of the digester treating a mix of municipal sludge (75% secondary sludge and 25% primary sludge).

The stability of the anaerobic digestion process was tested when municipal sludge co-digested with bakery waste. Stable performance was achieved and reported until the ratio of bakery waste to municipal sludge reached the range of 37% - 40% of bakery waste to 63%- 60% of municipal sludge based on COD analysis.

The stability of the induced bed reactor was tested with a higher ratio than was used in the batch reactors. The ratio of bakery waste to municipal sludge was 50:50% based on COD. Stable performance of the reactor was achieved with increasing the OLR from 1.85 kg COD $m^{-3}d^{-1}$ to 8.33 kg COD $m^{-3}d^{-1}$.

The existing mathematical model (ADM1) was developed to accurately predict the overall stability process and the digester performance in each mentioned scenario (the batch reactor and the induced bed reactor).

This research pointed out the following:

Bakery Waste is a strong candidate to be digested with municipal sludge for the reasons that were demonstrated through the research.

The modified ADM1 is a strong and useful model to be used for simulating the process, predicting the overall process stability and for decision making.

The IBR can handle high organic matter (up to 8.33 kg COD $m^{-3}d^{-1}$) and increase the range of stable performance over the fully mixed reactors.

CHAPTER 6

Engineering Significance

In this research, economic and environmental engineering significances based on the results of the ADM1 model and the experimental work will be outlined in the following paragraph:

The results of this research provided information regarding stability tools (stability index and optimized ADM1). In Chapter 2, the stability index could be used as a quick stability indicator, saving time, effort and money for the ecosystem that has been defined in the chapter.

The optimized ADM1 for both cases, fully mixed reactor and IBR, is a helpful tool to determine stability for the co-digestion of municipal sludge and bakery waste, the model will predict stability of the process in order to avoid any process inhibition or toxicity since the anaerobic digestion process is delicate and can be upset easily.

Huge amounts of bakery waste are capable to be treated using existing anaerobic digesters at wastewater facilities, especially when using induced bed reactors. This avoids the costs of building pre-treatment facilities to treat the bakery waste.

The process of co-digesting municipal sludge with bakery waste increased the quantity of biogas that the reactor is capable of producing. Also, the methane percentage was higher than when digesting municipal sludge alone. The methane percentage reported in this research was between 60-70% of the biogas instead of 55-60% when digesting municipal sludge.

Stable performance of the digester was achieved without adding any buffer to control the pH.

No grinding or mixing tools were used, again avoiding operational costs.

The process does not require construction of new digesters because the existing digesters for the wastewater plant easily treat it.

This research will help bakeries to have an alternative to discharge bakery waste. There is no need to construct a pretreatment unit which cost at least $10 million (Arsova 2010) for each bakery facility, moreover it will reduce the operational cost of adding buffer materials (sodium hydroxide) or grinding the waste. Aerobic treatment in the pretreatment units is expensive, in general, the operation cost for the pretreatment unit is $110 per ton of waste (Arsova 2010).

Another idea would be bringing sludge from municipal facilities to pretreatment units located at or near a bakery processor. This would be a good way to treat the BW without adding nutrients and buffer.

Environmental

Better understanding of the term “stability”

Better understanding the anaerobic digestion process by defining its stability for municipal sludge digestion, the research defines it as a constant rate between destroyed volatile solids and methane produced.

There are no fixed concepts that define process stability, each scenario may be different from another and needs some evaluation.

The research clarified that, municipal sludge, when mixed with bakery waste, will provide the required balanced nutrients for the microorganisms, and will lead to higher stability.

The results of the research pointed out the IBR ability to keep stable performance of the process over high range. However, the wastewater facilities commonly use fully mixed reactors not Induced Bed reactors. Using the results of this research opens the door about applying the techniques of the IBR in the wastewater facilities. Suggesting two digestion steps, one is fully mixed and the other is IBR reactor

CHAPTER 7

Recommendations

1) The Induced Bed Reactor actually includes 2 reactors, 20-30% is retained bacteria (Bed section), and fully mixed reactor (50-60%), then 10% of the reactor is gas. A more adequate ADM1 to predict the IBR performance will require two-stages of modeling. One stage for the bed section and one stage for the mixed section
2) Microbial analysis for the population is required in-order to understand the shift in the microorganisms. DNA and qPCR for the Methanogenesis to know the participations of hydrogenotrophic and acetoclastic Methanogenesis.

3) In this research, the role of hydrogenotrophic methanogenesis was pointed out. Digesting the bakery waste with municipal sludge may enhance hydrogenotrophic methanogenesis and, accordingly, there will be a good opportunity for enhancing the production of hydrogen gas from municipal facilities as described in Figure 39

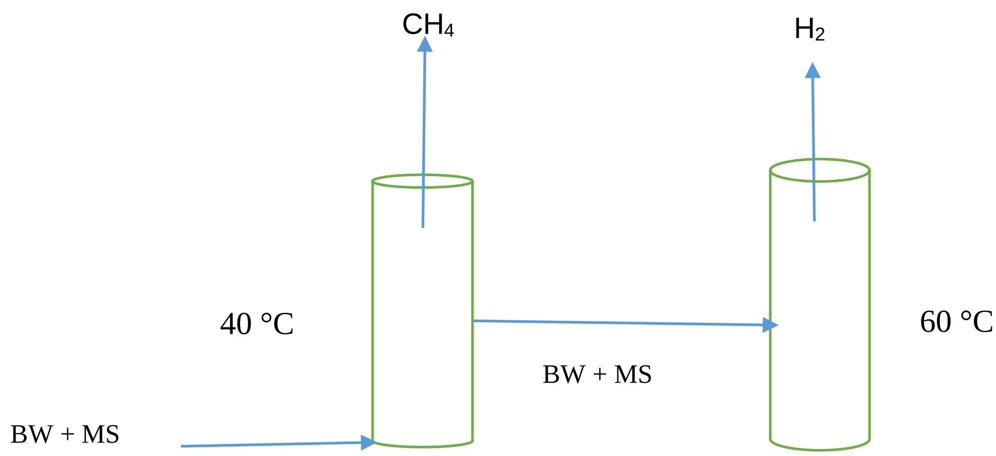


Figure 39. Two stages digestion for hydrogen production

CHAPTER 8

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APPENDICES

Appendix A:

Monte Carlo Simulation

Sensitivity analysis using Monte Carlo simulation was run for 10000 iterations to test the stable performance of the IBR using the modified model, in case of HRT= 12 days, HRT= 9 days and HRT = 6 days. The input values for the Monte Carlo simulation are shown in Table 13. The inputs basically are the average and standard deviation for the carbohydrates, lipids and proteins, also the suggested and the modified values for the hydrolysis model coefficients.

The Monte Carlo simulation when HRT= 12 days (Figure 38) shows normal distribution for all the stability indicators (pH, Q (m^3/d), CH_4 (%) and the TVFA (mg/L). The average values were (pH~7.26, Q~0.11 (m^3/d), CH_4 ~0.665% of the biogas (Q), and TVFA ~ 147 (mg/L). The 10000 iterations demonstrated 100% stable performance for the IBR in this case.

The Monte Carlo simulation when HRT= 9 days (Figure 39) shows normal distribution for all the stability parameters (pH, Q (m^3/d), CH_4 (%) and the TVFA (mg/L). The average values were (pH~7.26, Q~0.15 (m^3/d), CH_4 ~ (0.65%), TVFA ~ (220 mg/L)). The 10000 iterations demonstrated 100% stable performance for the IBR in this case.

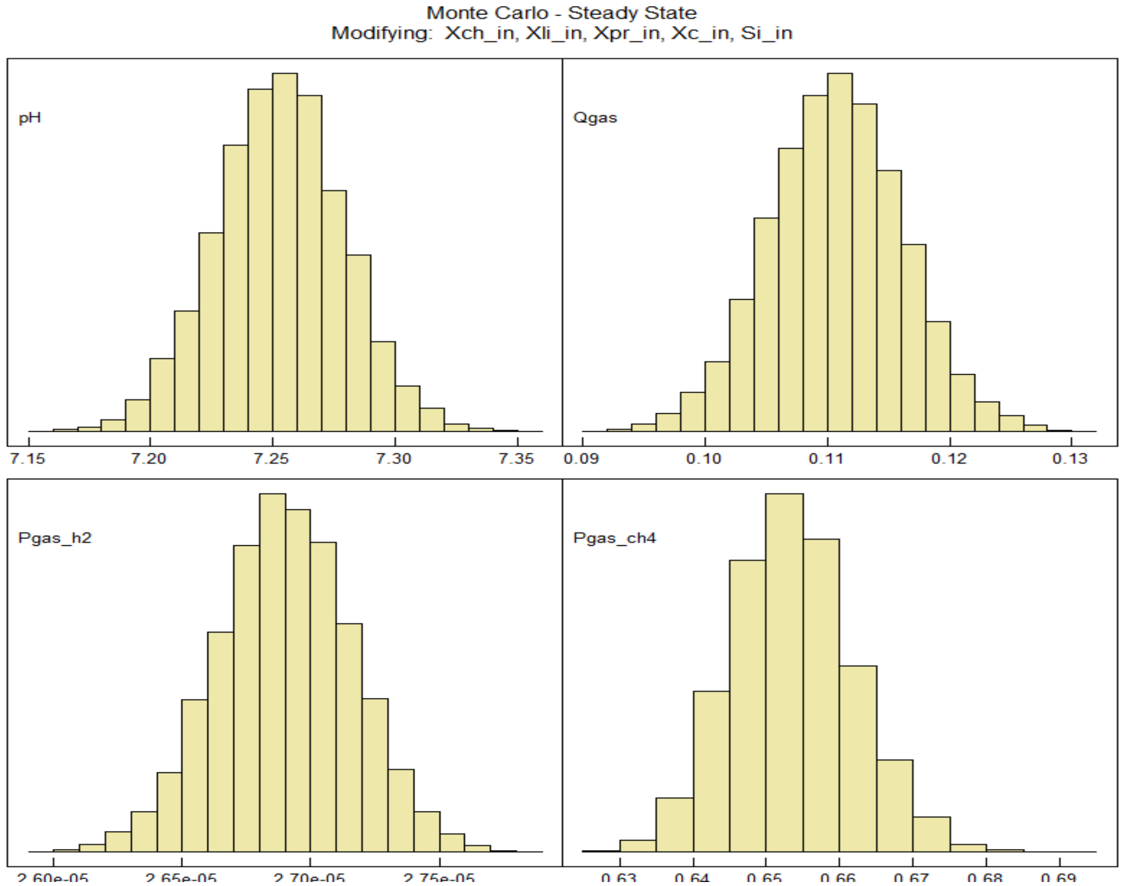
The Monte Carlo simulation when HRT= 6 days (Figure 40) shows major changes in the digester performance. The results show 65% (the area under the curve) is the possibility of the digester failure when HRT= 6 days, while 35% is the stable performance of the digester.

Figure 39 - 41 shows the simulations (histograms) from Monte Carlo analysis for HRT= 12, 9 and 6 days respectively.

Table 13. The values for the Monte Carlo simulation

COD	Mean ± SD (g/L)	Model coefficients	Initial Value (d^{-1})	Modified Value (d^{-1})
Carbohydrates COD	25.63 ±1.71	Carbohydrates Hydrolysis	10	13
Proteins COD	12.06 ± 0.78	Carbohydrates Lipids	9	10
Lipids COD	7.54 ± 0.51	Carbohydrates Proteins	8.6	10.5
Inert Compound COD	3 ± 0.36			
Inert Soluble COD	2 ± 0.11			

HRT= 12 days


Monte Carlo - Steady State
Modifying: Xch_in, Xli_in, Xpr_in, Xc_in, Si_in
pH
7.15
7.20
7.25
7.30
7.35
Qgas
0.09
0.10
0.11
0.12
0.13
Pgas_h2
2.60e-05
2.65e-05
2.70e-05
2.75e-05
Pgas_ch4
0.63
0.64
0.65
0.66
0.67
0.68
0.69

The correction was done because the ADM1 assumed the partial pressure of the gas = 1 atm.

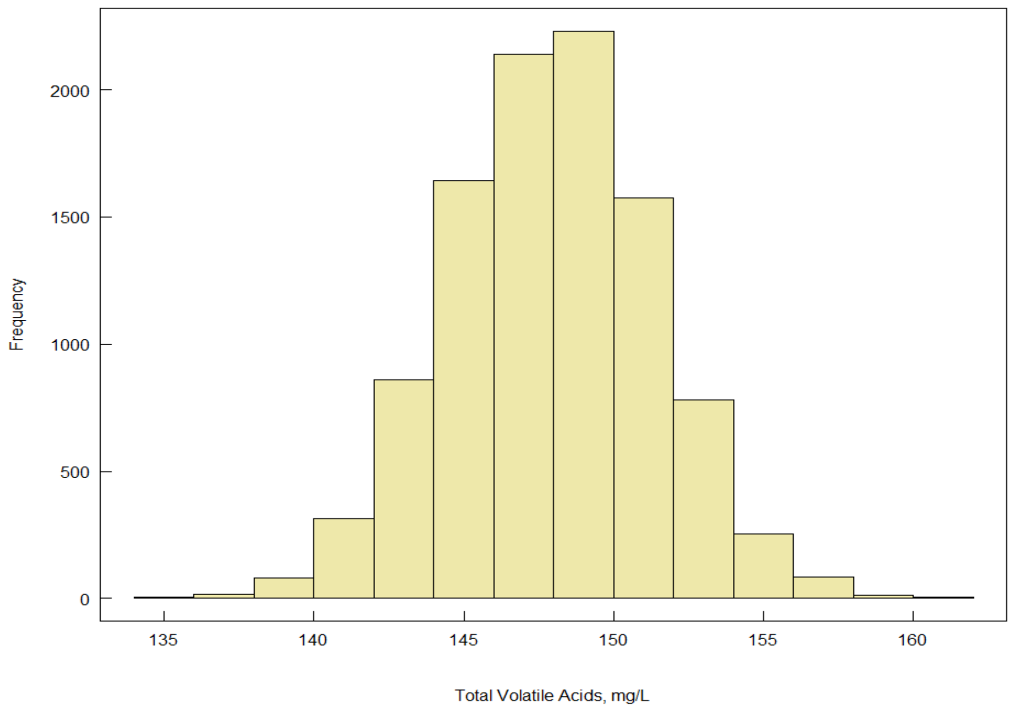
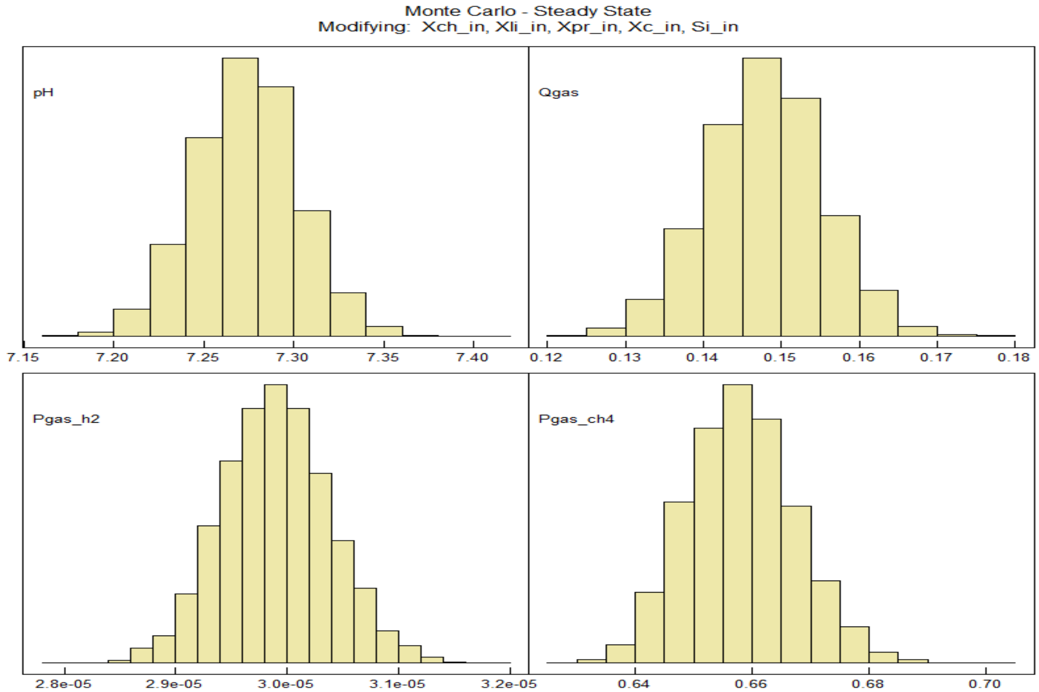


Figure 40. Monte-Carlo analysis (histograms) for the stability indicators (pH, Q(m^3/d), CH_4(%) , and total volatile fatty acids (mg/L) in case of HRT= 12 days.

HRT= 9 days



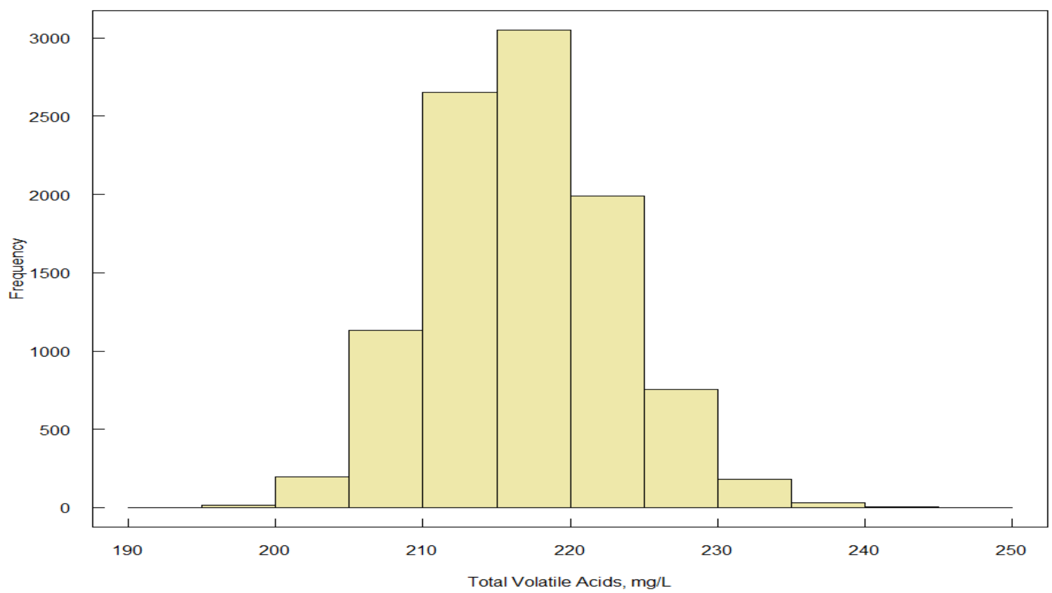
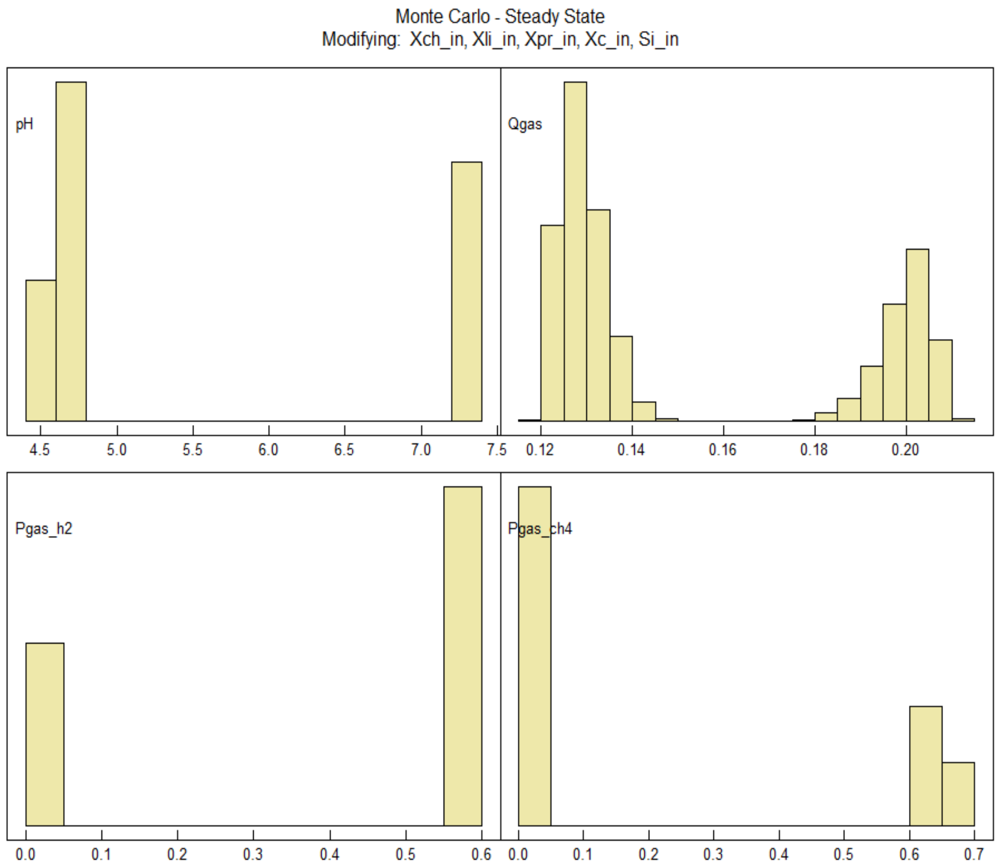


Figure 41. Monte-Carlo simulations (histograms) for the stability indicators (pH, Q (m^3/d) CH_4(%) and total volatile fatty acids (mg/L) in case of HRT= 9 days


Monte Carlo - Steady State
Modifying: Xch_in, Xli_in, Xpr_in, Xc_in, Si_in
pH
Qgas
Pgas_h2
Pgas_ch4
4.5
5.0
5.5
6.0
6.5
7.0
7.5
0.12
0.14
0.16
0.18
0.20
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7

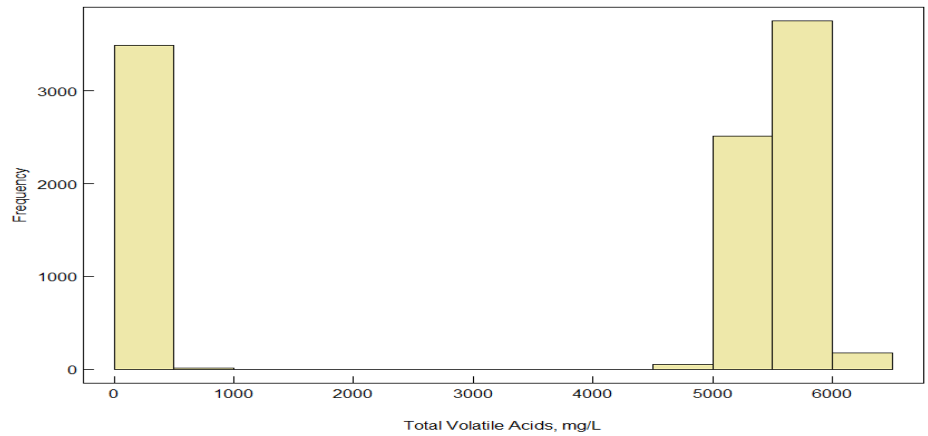


Figure 42. Monte-Carlo analysis (histograms) for the stability indicators (pH, Q(m^3/d), CH_4(%) and the total volatile fatty acids (mg/L) in case of HRT= 6 days

Appendix B

(The R code for the modified ADM1)

The R code for the optimized model for the applications of the co-digestion of bakery waste and municipal sludge. In-order to run the model, Copy the code and paste it in R software programing. The following instructions clarifies the model inputs for the code in R:

1. Determine the total COD for the substrate for the influent

2. Divided the Total COD between Carbohydrates, Lipids and Proteins based on its ratios inside the substrate (Xch_in (Kg/M^3), Xlip_in (Kg/M3 and Xpr_in (M^3/d), and the non-biodegradable fraction of the COD, soluble and particulates (Si_in=; Xc_in)

3. Determine the total volume of the reactor, determine the liquid volume and the gas volume (Vliq= M^3, Vgas=M^3)

4. Determine the flow rate Q (M^3/d) = Vliq (M^3)/(day)

5. Put the temperature of the reactor in Kelvin units (Ttop=°K)

The following diagram estimate the COD fraction for the ADM1 model:

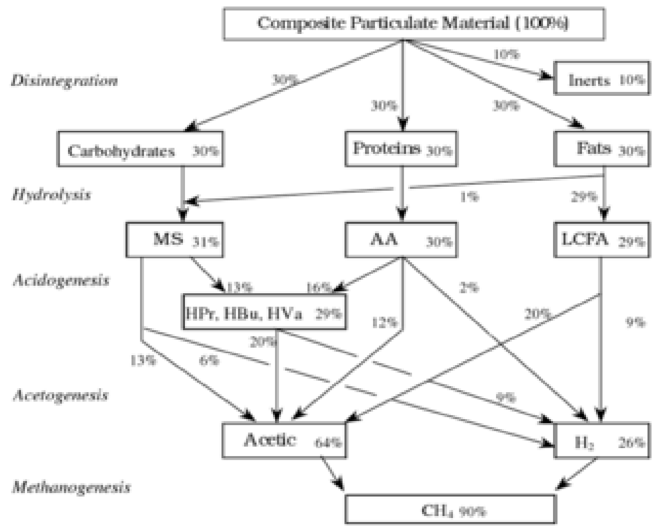


Figure 43. COD flux for the ADM1, adapted from (Batstone et al. 2002)

The ADM1 code using R software for the case of MS co-digested with BW:

```
#(t:independent variable, state: list of state variables, par:constants)
ADM1_C<-function(t,state,parameters){
with(as.list(c(state,parameters)), {
#Algebraic equ
 Snh4=Sin-Snh3
 Sco2=Sic-Shco3_m
 Z=Scation+Snh4-Shco3_m-Sac_m/64-Spro_m/112-Sbu_m/160-Sva_m/208-Sanion
 Kw=(exp(55900/(R*100)*(1/Tbase-1/Top)))*(10^(-14))
 Sh=-Z*.5+.5*sqrt(Z^2+4*Kw)
#pH
pH = -log10(Sh)
#inhibition factors
IpH_aa<- if ( pH<pHuL_aa) exp(-3*((pH-pHuL_aa)/(pHuL_aa-pHlL_aa))^2) else 1
IpH_ac<- if ( pH<pHuL_ac) exp(-3*((pH-pHuL_ac)/(pHuL_ac-pHlL_ac))^2) else 1
```

```
IpH_h2<- if ( pH<pHuL_h2) exp(-3*((pH-pHuL_h2)/(pHuL_h2-pHlL_h2))^2) else 1
Iin_lim = 1/(1+Ks_in/Sin)
Ih2_fa = 1/(1+Sh2/Ki_h2_fa)
Ih2_c4 = 1/(1+Sh2/Ki_h2_c4)
Ih2_pro = 1/(1+Sh2/Ki_h2_pro)
Inh3 = 1/(1+Snh3/Ki_nh3)
I5=I6=IpH_aa*Iin_lim
I7=IpH_aa*Iin_lim*Ih2_fa
I8=I9=IpH_aa*Iin_lim*Ih2_c4
I10=IpH_aa*Iin_lim*Ih2_pro
I11=IpH_ac*Iin_lim*Inh3
I12=IpH_h2*Iin_lim
#process rates
 P1=Kdis*Xc
P2=Khyd_ch*Xch
P3=Khyd_pr*Xpr
P4=Khyd_li*Xli
P5=Km_su*Ssu/(Ks_su+Ssu)*Xsu*I5
P6=Km_aa*Saa/(Ks_aa+Saa)*Xaa*I6
P7=Km_fa*Sfa/(Ks_fa+Sfa)*Xfa*I7
P8=Km_c4*Sva/(Ks_c4+Sva)*Xc4*Sva/(Sbu+Sva+1e-6)*I8
P9=Km_c4*Sbu/(Ks_c4+Sbu)*Xc4*Sbu/(Sva+Sbu+1e-6)*I9
P10=Km_pro*Spro/(Ks_pro+Spro)*Xpro*I10
P11=Km_ac*Sac/(Ks_ac+Sac)*Xac*I11
P12=Km_h2*Sh2/(Ks_h2+Sh2)*Xh2*I12
P13=Kdec_xsu*Xsu
P14=Kdec_xaa*Xaa
P15=Kdec_xfa*Xfa
```

```
P16=Kdec_xc4*Xc4
P17=Kdec_xpro*Xpro
P18=Kdec_xac*Xac
P19=Kdec_xh2*Xh2
#inorganic carbon
S1=-Cxc+FsI_xc*CsI+Fch_xc*Cch+Fpr_xc*Cpr+Fli_xc*Cli+FxI_xc*CxI
S2=-Cch+Csu
S3=-Cpr+Caa
S4=-Cli+(1-Ffa_li)*Csu+Ffa_li*Cfa
S5=-Csu+(1-Ysu)*(Fbu_su*Cbu+Fpro_su*Cpro+Fac_su*Cac)+Ysu*Cbac
S6=-Caa+(1-Yaa)*(Fva_aa*Cva+Fbu_aa*Cbu+Fpro_aa*Cpro+Fac_aa*Cac)+Yaa*Cbac
S7=-Cfa+(1-Yfa)*0.7*Cac+Yfa*Cbac
S8=-Cva+(1-Yc4)*.54*Cpro+(1-Yc4)*.31*Cac+Yc4*Cbac
S9=-Cbu+(1-Yc4)*.8*Cac+Yc4*Cbac
S10=-Cpro+(1-Ypro)*.57*Cac+ Ypro*Cbac
S11=-Cac+(1-Yac)*Cch4+ Yac*Cbac
S12=(1-Yh2)*Cch4+ Yh2*Cbac
S13=-Cbac+Cxc
#acid-base rates:
Pa_4=Ka_bva*(Sva_m*(Ka_va+Sh)-Ka_va*Sva)
Pa_5=Ka_bbu*(Sbu_m*(Ka_bu+Sh)-Ka_bu*Sbu)
Pa_6=Ka_bpro*(Spro_m*(Ka_pro+Sh)-Ka_pro*Spro)
Pa_7=Ka_bac*(Sac_m*(Ka_ac+Sh)-Ka_ac*Sac)
Ka_co2=10^(-6.35)*exp(7646/(R*100)*(1/Tbase-1/Top))
Pa_10=Ka_bco2*(Shco3_m*(Ka_co2+Sh)-Ka_co2*Sic)
Ka_in=10^(-9.25)*exp(51965/(R*100)*(1/Tbase-1/Top))
Pa_11=Ka_bin*(Snh3*(Ka_in+Sh)-Ka_in*Sin)
#gas transfer equ&as transfer rates
```

```
Pgas_h2=Sgas_h2*R*Top/16

Pgas_ch4=Sgas_ch4*R*Top/64

Pgas_co2=Sgas_co2*R*Top

Kh_h2=(7.8e-4)*exp(-4180/(R*100)*(1/Tbase-1/Top))

Pt_8=KL*(Sh2-16*Kh_h2*Pgas_h2)

Kh_ch4=0.0014*exp(-14240/(R*100)*(1/Tbase-1/Top))

Pt_9=KL*(Sch4-64*Kh_ch4*Pgas_ch4)

Kh_co2=0.035*exp(-19410/(R*100)*(1/Tbase-1/Top))

Pt_10=KL*(Sco2-Kh_co2*Pgas_co2)

Pgas_h2o=0.0313*exp(5290*(1/Tbase-1/Top))

Qgas = R*Top/(Patm-Pgas_h2o)*Vliq*(Pt_8/16+Pt_9/64+Pt_10)

#Components dff equ.

dSsu = tau*Ssu_in-tau*Ssu+(P2+(1-Ffa_li)*P4-P5)#C1  components

dSaa = tau*Saa_in-tau*Saa+(P3-P6)#C2

dSfa = tau*Sfa_in-tau*Sfa+(Ffa_li*P4-P7)#C3

dSva = tau*Sva_in-tau*Sva+((1-Yaa)*Fva_aa*P6-P8)#C4

dSbu = tau*Sbu_in-tau*Sbu+((1-Ysu)*Fbu_su*P5+(1-Yaa)*Fbu_aa*P6-P9)#C5

dSpro= tau*Spro_in-tau*Spro+((1-Ysu)*Fpro_su*P5+(1-Yaa)*Fpro_aa*P6+(1-
Yc4)*.54*P8-P10)#C6

dSac = tau*Sac_in-tau*Sac+((1-Ysu)*Fac_su*P5+(1-Yaa)*Fac_aa*P6+.50*(1-Yfa)*P7

        +.20*(1-Yc4)*P8+.4*(1-Yc4)*P9+.50*(1-Ypro)*P10-P11)#C7

dSh2 = tau*Sh2_in-tau*Sh2+((1-Ysu)*Fh2_su*P5

        +(1-Yaa)*Fh2_aa*P6+.50*(1-Yfa)*P7+.26*(1-Yc4)*P8+.6*(1-Yc4)*P9+.50*(1-
Ypro)*P10

        -P12-Pt_8)#C8

dSch4 = tau*Sch4_in-tau*Sch4+((1-Yac)*P11+(1-Yh2)*P12-Pt_9)#C9

dSic  = tau*Sic_in-tau*Sic-
(sum(S1*P1,S2*P2,S3*P3,S4*P4,S5*P5,S6*P6,S7*P7,S8*P8,S9*P9,S10*P10,S11*P11,
S12*P12)+S13*(P13+P14+P15+P16+P17+P18+P19))-Pt_10 #C10
```

```
dSin  =  tau*Sin_in-tau*Sin-Ysu*Nbac*P5+(Naa-Yaa*Nbac)*P6-Yfa*Nbac* P7-
Yc4*Nbac*P8-Yc4*Nbac*P9-Ypro*Nbac*P10-Yac*Nbac*P11-Yh2*Nbac*

P12+(Nbac-Nxc)*sum(P13,P14,P15,P16,P17,P18,P19)+(Nxc-FxI_xc*Ni-FsI_xc*Ni-
Fpr_xc*Naa)*P1 #C11

dSi   = tau*Si_in-tau*Si+FsI_xc*P1   #C12

dXc   = tau*Xc_in-tau*Xc +(-P1+sum(P13,P14,P15,P16,P17,P18,P19))  #C13

dXch = tau*Xch_in-tau*Xch +(Fch_xc*P1-P2)   #C14

dXpr = tau*Xpr_in-tau*Xpr +(Fpr_xc*P1-P3)  #C15

dXli = tau*Xli_in-tau*Xli +(Fli_xc*P1-P4)  #C16

dXsu = tau*Xsu_in-tau*Xsu +(Ysu*P5-P13)  #C17

dXaa = tau*Xaa_in-tau*Xaa +(Yaa*P6-P14)  #C18

dXfa =tau*Xfa_in-tau*Xfa +(Yfa*P7-P15)  #C19

dXc4 =tau*Xc4_in-tau*Xc4 +(Yc4*P8+Yc4*P9-P16)  #C20

dXpro =tau*Xpro_in-tau*Xpro +(Ypro*P10-P17)  #C21

dXac =tau*Xac_in-tau*Xac +(Yac*P11-P18)  #C22

dXh2 =tau*Xh2_in-tau*Xh2 +(Yh2*P12-P19)  #C23

dXi =tau*Xi_in-tau*Xi +(FxI_xc*P1)  #C24

dScation =tau*Scation_in-tau*Scation  #C25  cations and anions

dSanion =tau*Sanion_in-tau*Sanion    #C26

dSva_m = -Pa_4  #C27   ion states

dSbu_m = -Pa_5  #C28

dSpro_m = -Pa_6  #C29

dSac_m = -Pa_7   #C30

dShco3_m = -Pa_10 #C31

dSnh3 = -Pa_11   #C32

dSgas_h2 =-Sgas_h2*Qgas/Vgas+Pt_8*Vliq/Vgas    #33   gas phase differential equ.

dSgas_ch4 =-Sgas_ch4*Qgas/Vgas+Pt_9*Vliq/Vgas    #34

dSgas_co2 =-Sgas_co2*Qgas/Vgas+Pt_10*Vliq/Vgas    #35

list(c(dSsu,dSaa,dSfa,dSva,dSbu,dSpro,dSac,dSh2,dSch4,dSic,dSin,dSi,dXc,dXch,dXpr,
```

```
dXli,dXsu,dXaa,dXfa,dXc4,dXpro,dXac,dXh2,dXi,dScation,dSanion,dSva_m,dSbu_m,dSpro_m

,dSac_m,dShco3_m,dSnh3,dSgas_h2,dSgas_ch4,dSgas_co2))

# calculate pH Pgas_h2,Pgas_ch4,Pgas_co2?

require(deSolve) # external package1

Q = 0.0090; Vliq=0.054; Vgas=0.006

tau=Q/Vliq;

#parameters' values, change values based on different digestion

Ffa_li=0.95;Yaa=0.08;Fva_aa=0.23;Ysu=0.1;Fbu_su=0.13;Fbu_aa=0.26;Fpro_su=0.27;Fpro_aa=0.05;Yc4=0.06;

Fac_su=0.41;Fac_aa=0.4;Yfa=0.06;Ypro=0.04;Fh2_su=0.19;Fh2_aa=0.06;Yac=0.05;Yh2=0.06;Nbac=0.08/14;

Naa =0.007; Nxc=0.0376/14;FxI_xc=0.2;Ni=0.06/14;FsI_xc=0.1;Fpr_xc=0.2;Fch_xc=0.2;Fli_xc=0.3;

Kdis=0.5;Khyd_ch=13;Khyd_pr=10;Khyd_li=10.5;Km_su=30;Ks_su=0.5;Km_aa=50;Ks_aa=0.3;Km_fa=6;Ks_fa=0.4;

Km_c4=20;Ks_c4=0.2;Km_pro=13;Ks_pro=0.1;Km_ac=8;Ks_ac=0.15;Km_h2=35;Ks_h2=7e-6;

Kdec_xsu= Kdec_xaa= Kdec_xfa=Kdec_xc4= Kdec_xpro= Kdec_xac= Kdec_xh2=0.02;Cxc=0.02786;CsI=0.03;

Cch=0.0313;Cpr=0.03;Cli=0.022;CxI=0.03;Csu=0.0313;Caa=0.03;Cbu=0.025;Cpro=0.0268;Cac=0.0313;

Cbac =0.0313;Cva=0.024;Cfa=0.0217;Cch4=0.0156;pHuL_aa=5.5;pHlL_aa=4;pHuL_ac=7;pHlL_ac=6;

pHuL_h2=6;pHlL_h2=5;Ks_in=1e-4;Ki_h2_fa=5e-6;Ki_h2_c4=1e-5;Ki_h2_pro=3.5e-6;Ki_nh3=0.0018;

Ka_bva= Ka_bbu= Ka_bpro= Ka_bac= Ka_bco2= Ka_bin=1e10;Ka_va=10^(-4.86);

Ka_bu=10^(-4.82);Ka_pro=10^(-4.88);Ka_ac=10^(-4.76);KL=200;

R=0.083145;Tbase=298.15;Top=308.15;Pbar= 1.013; Kw=(exp(55900/(R*100)*(1/Tbase-1/Top)))*(10^(-14))

Ka_co2=10^(-6.35)*exp(7646/(R*100)*(1/Tbase-1/Top))

Ka_in=10^(-9.25)*exp(51965/(R*100)*(1/Tbase-1/Top))
```

```
Kh_h2=(7.8e-4)*exp(-4180/(R*100)*(1/Tbase-1/Top))

Kh_ch4=0.0014*exp(-14240/(R*100)*(1/Tbase-1/Top))

Kh_co2=0.035*exp(-19410/(R*100)*(1/Tbase-1/Top))

Pgas_h2o=0.0313*exp(5290*(1/Tbase-1/Top))

#input values

Ssu_in=0.01;Saa_in=0.001;Sfa_in=0.001; Sva_in=0.001; Sbu_in=0.001; Spro_in=0.001;

Sac_in=0.001; Sh2_in=1e-8; Sch4_in=1e-5; Sic_in=0.01; Sin_in=0.02; Si_in=1.2;
Xc_in=5.2;

Xch_in=24.50; Xpr_in=7.9; Xli_in=13.90; Xsu_in=0.00; Xaa_in=0.01; Xfa_in=0.001;
Xc4_in=0.01;

Xpro_in=0.01; Xac_in=0.01; Xh2_in=0.01; Xi_in=16; Scation_in=0.04; Sanion_in=0.02

#states initial condition, liquid within the digester, not the input

state=c(Ssu=0.011,Saa=0.005,Sfa=0.093, Sva=0.013, Sbu=0.013, Spro=0.0153,
Sac=0.193, Sh2=2.3e-7,

Sch4=0.055, Sic=0.04, Sin=0.01, Si=0.02, Xc=0.3, Xch=0.026, Xpr=0.1, Xli=0.03,
Xsu=0.4, Xaa=1.17,

Xfa=0.20, Xc4=0.41, Xpro=0.137, Xac=0.7, Xh2=0.317, Xi=5, Scation=0.04,
Sanion=0.02,

Sva_m=0.0601, Sbu_m=0.0905,Spro_m=0.13, Sac_m=0.159, Shco3_m=0.0090,

Snh3=0.0165, Sgas_h2=0.03, Sgas_ch4=0.029, Sgas_co2=0.0378)

#parameters

parameters=c(Ffa_li= Ffa_li,Yaa= Yaa,Fva_aa= Fva_aa,Ysu= Ysu,Fbu_su=
Fbu_su,Fbu_aa= Fbu_aa,

Fpro_su= Fpro_su,Fpro_aa= Fpro_aa,Yc4= Yc4,Fac_su= Fac_su,Fac_aa= Fac_aa,Yfa=
Yfa,Ypro= Ypro,

Fh2_su= Fh2_su,Fh2_aa= Fh2_aa,Yac= Yac,Yh2= Yh2,Nbac= Nbac,Naa = Naa,Nxc=
Nxc,FxI_xc= FxI_xc,

Ni= Ni,FsI_xc= FsI_xc,Fpr_xc= Fpr_xc,Fch_xc= Fch_xc,Fli_xc= Fli_xc,Kdis=
Kdis,Khyd_ch= Khyd_ch,

Khyd_pr= Khyd_pr,Khyd_li= Khyd_li,Km_su= Km_su,Ks_su= Ks_su,Km_aa=
Km_aa,Ks_aa= Ks_aa,Km_fa= Km_fa,
```

```
Ks_fa= Ks_fa,Km_c4= Km_c4,Ks_c4= Ks_c4,Km_pro= Km_pro,Ks_pro=
Ks_pro,Km_ac= Km_ac,Ks_ac= Ks_ac,

Km_h2= Km_h2,Ks_h2= Ks_h2,Kdec_xsu=Kdec_xsu, Kdec_xaa= Kdec_xaa,
Kdec_xfa= Kdec_xfa,

Kdec_xc4= Kdec_xc4, Kdec_xpro= Kdec_xpro, Kdec_xac=Kdec_xac, Kdec_xh2=
Kdec_xh2,Cxc= Cxc,

CsI= CsI,Cch= Cch,Cpr= Cpr,Cli= Cli,CxI= CxI,Csu= Csu,Caa= Caa,Cbu= Cbu,

Cpro= Cpro,Cac= Cac,Cbac = Cbac,Cva= Cva,Cfa= Cfa,Cch4= Cch4,pHuL_aa=
pHuL_aa,pHlL_aa= pHlL_aa,

pHuL_ac= pHuL_ac,pHlL_ac= pHlL_ac, pHuL_h2= pHuL_h2,pHlL_h2=
pHlL_h2,Ks_in= Ks_in,Ki_h2_fa= Ki_h2_fa,

Ki_h2_c4= Ki_h2_c4,Ki_h2_pro= Ki_h2_pro,Ki_nh3= Ki_nh3, Ka_bva= Ka_bva,
Ka_bbu= Ka_bbu,

Ka_bpro= Ka_bpro, Ka_bac= Ka_bac, Ka_bco2= Ka_bco2, Ka_bin= Ka_bin, Ka_va=
Ka_va,

Ka_bu= Ka_bu,Ka_pro= Ka_pro,Ka_ac= Ka_ac,KL= KL,R= R,

Tbase=Tbase,Top= Top,Patm= Patm,

Kh_h2= Kh_h2, Kh_ch4= Kh_ch4,Kh_co2= Kh_co2,Ka_in=
Ka_in,Pgas_h2o=Pgas_h2o)


#extract pH

getpH <- function(state) {

with(as.list(c(state,parameters)), {

Snh4=Sin-Snh3

Z=Scation+Snh4-Shco3_m-Sac_m/64-Spro_m/112-Sbu_m/160-Sva_m/208-Sanion

Sh=-Z*0.5+0.5*sqrt(Z^2+4*Kw)

pH <- -log10(Sh*0.6)})

}


#extract Qgas

getQgas <- function(state) {
```

```
  with(as.list(c(state,parameters)), {
Sco2=Sic-Shco3_m
Pgas_h2=Sgas_h2*R*Top/16
Pgas_ch4=Sgas_ch4*R*Top/64
Pgas_co2=Sgas_co2*R*Top
Pt_8=KL*(Sh2-16*Kh_h2*Pgas_h2)
Pt_9=KL*(Sch4-64*Kh_ch4*Pgas_ch4)
Pt_10=KL*(Sco2-Kh_co2*Pgas_co2)
Qgas = R*Top/(Patm-Pgas_h2o)*Vliq*(Pt_8/16+Pt_9/64+Pt_10) })
}
# extract Pgas_h2/ch4/co2
getPgas_h2 <- function(state) {
with(as.list(c(state,parameters)), {
   Pgas_h2=Sgas_h2*R*Top/16})
}
getPgas_ch4 <- function(state) {
with(as.list(c(state,parameters)), {
Pgas_ch4=Sgas_ch4*R*Top/64})
}
getPgas_co2 <- function(state) {
with(as.list(c(state,parameters)), {
Pgas_co2=Sgas_co2*R*Top})
}
state.pH <- getpH(state=state)
state.Qgas <- getQgas(state=state)
state.Pgas_h2 <- getPgas_h2(state=state)
state.Pgas_ch4 <- getPgas_ch4(state=state)
state.Pgas_co2 <- getPgas_co2(state=state)
```

```
#doesn't need it, the initial value
times <- seq(0,20,by = 1)
out <- as.data.frame(ode(y = state,times = times,func = ADM1_C,parms = parameters))
out$pH <- getpH(state=out)
out$Qgas<-getQgas(state=out)
out$Pgas_h2<-getPgas_h2(state=out)
out$Pgas_ch4<-getPgas_ch4(state=out)
out$Pgas_co2<-getPgas_co2(state=out)
# plot the output
par(mfrow=c(4,5),mar=c(0,0,0,0),mgp=c(2.5,.5,0),oma=c(5,4,2,1),las=1,tcl=.25,cex.axis
=.75)
iplt <<- 1        ##1:n, 1 is the time
lapply(2:21,function(ix) {
  x = out[,ix]; tx <- names(out)[ix]
  plot(x~out$time,type='l',xaxt='n',ylab='')
  if(iplt > 15) {
    axis(1,labels=T)
  }
  else {
 axis(1,labels=F)
  }
  u <- par('usr'); dy = diff(u[3:4])/10
text(0,par('usr')[4]-dy,labels=tx,pos=4)
cat(iplt,tx,'\n')        ###\n huanhang,
  iplt <<- iplt + 1
} )
mtext('Time, days',side=1,outer=T,line=3)
mtext('Constituent value',side=2,line=2,las=0,outer=T)
windows()
```

```
par(mfrow=c(4,5),mar=c(0,0,0,0),mgp=c(2.5,.5,0),oma=c(5,4,2,1),las=1,tcl=.25,cex.axis
=.75)
iplt <<- 1          ##1:n, 1 is the time
lapply(22:41,function(ix) {
  x = out[,ix]; tx <- names(out)[ix]
plot(x~out$time,type='l',xaxt='n',ylab='')
  if(iplt > 15) {
    axis(1,labels=T)
  }
  else {
    axis(1,labels=F)
  }
 u <- par('usr'); dy = diff(u[3:4])/10
 text(0,par('usr')[4]-dy,labels=tx,pos=4)
cat(iplt,tx,'\n')          ###\n huanhang,
iplt <<- iplt + 1
} )
write.table(out, file = "18 HRT.csv", sep = ",", col.names = NA,
qmethod = "double")
write.csv(x, file = "foo.csv")
read.csv("foo.csv", row.names = 1)
mtext('Time, days',side=1,outer=T,line=3)
mtext('Constituent value',side=2,line=2,las=0,outer=T)
```

CIURRICULUM VITAE

Morris Demitry

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Specialties and Skills

Water Quality and Wastewater Management
Anaerobic Digestion

Biochemical Techniques **Statistical Data Analysis** **Mathematical Model Development**

EDUCATION

PhD of Environmental Engineering- Utah State University, Logan UT.
May- 2016

- Thesis: The Stability of the Anaerobic Digestion Process

Master of Environmental Engineering- Utah State University**,** Logan, UT. December**- 2011**

- Thesis: Surface water quality in the Nile River

BSC of Civil Engineering – University of Khartoum
August -2001

- Major: Concrete Technology

ENGINEERING EXPERIENCE

Engineer, Central Weber Improvement District **May 2013- May 2015**

- Operate and monitor the anaerobic digestion process in full-scale for biogas enhancement
- Develop a mathematical computer model to simulate the performance of the anaerobic digestion process at the facility
- Test and evaluate the stability of the anaerobic digestion process
- Biogas enhancement using Bakery Waste co-digested with municipal wastewater

- Monitor day-to-day operations of the plant resulting in improving efficiency and reducing operating cost
- Reduced the wastewater treatment cost by 20% using new coagulants material
- Consistently monitor treated sewage for composting purposes
- Characterizing the water quality of reclaimed wastewater
- Involving with the recovery of resources from wastewater
- Monitoring the overall wastewater treatment process inside the plant using SCADA programming software
- Communicate with the wastewater director and engineers to advise about the project and operations

PROJECTS

Graduate Research Assistant, Utah Water Research Laboratory

- Food Engineering lab manager to help undergraduate and graduate students to complete experiments
- Familiar with using Gas Chromatograph, HACH Methods for Chemical Oxygen demand, and Volatile Fatty Acids measurements
- Using laboratory - scale reactors to investigate the potential for recovering energy from wastewater
- Investigating the microbial communities involved in wastewater treatment processes that recovery energy resources
- Develop the Anaerobic Digestion Model Number 1 (ADM1) to accurately predict the process of the co-digestion of Bakery waste with Municipal Sludge
- Understanding hazards waste treatment, storage and disposal requirements (OSHA)
- Develop a new method to produce hydrogen gas using Induced Bed Reactors (IBR)
- Performing data analysis to performing reports that explain findings using engineering tools to collect, measure and analyze environmental data
- Assisted the teaching of the courses-Water Quality and Wastewater Biological Treatment
- Guided three students in their thesis research assisting with statistics and experiments

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OTHER RELATED EXPERIANCE

Graduate Research Assistant, Utah Water Research Laboratory, Logan, UT
2009-2011

- Tested and examined inexpensive methods for the household water treatment
- Participated in data collection and modeling for water quality constituents, and air quality.
- Focusing on successful assessment of risk management skills including sampling, designing, and decision making of environmental and hydraulic systems
- Evaluate new techniques for the water desalination using reverse osmosis

Senior Contract Administrator/Estimator March 2007 – July 2009

Biwater Pty ltd, Khartoum Sudan

London-United Kingdom

- Prepared tender documents for three infrastructure projects: Intake Structure, Sludge Storage (water treatment plant with capacity of 250,000 m^3 per day), and a Circular Reservoir Tank
- Reviewed the design drawings and specifications, prepared form of tender, provided assistance during tendering, evaluated tenders and prepared bid evaluation reports listing the qualified contractors for each project.
- Assisted in the preparation of the cost estimate report for each project including tracking of expenditures
- Initiated the construction start-up meetings with the contractors and attended site meetings on bi-weekly basis. Prepared meeting minutes and circulated to all parties involved
- Assessed, reviewed tenders and prepared cost estimates.
- Inspected and prepared daily progress reports and time schedule
- Prepared and managed the project schedule and budget of up to $ 2 million

AWARDS AND CERTIFICATES:

- Water Environmental Association of Utah WEAU awards - **November -2013**
- OSHA Certified **May -2013**
- Fundamentals of Engineering-passed **April - 2013**
- Ivanhoe foundation awards

COMPUTER SKILLS AND LANGUAGES

- Anaerobic Digestion Model Number 1 (ADM1)
- R programing for statistical computing
- Primevera for project management
- MS Office, GIS, Internet Research