2020-03-18

ANAEROBIC CO- DIGESTION OF CAFETERIA LEFTOVER FOOD AND TOILET WASTES FOR BIOGAS PRODUCTION AND KINETIC EXPERIMENT

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Master thesis

ANAEROBIC CO - DIGESTION OF CAFETERIA LEFTOVER FOOD AND TOILET WASTES FOR BIOGAS PRODUCTION AND KINETIC EXPERIMENT

BAHIR DAR INSTITUTE OF TECHNOLOGY, BAHIR DAR UNIVERSITY, BAHIR DAR, ETHIOPIA

FACULTY OF CHEMICAL AND FOOD ENGINEERING FACULTY

JUNE, 2016

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ANAEROBIC CO - DIGESTION OF CAFETERIA LEFTOVER FOOD AND TOILET WASTES FOR BIOGAS PRODUCTION AND KINETIC EXPERIMENT

A thesis Submitted to Chemical Engineering Department in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering (Specialized in Process Engineering)

A Thesis Presented at Bahir Dar Institute of Technology, Bahir Dar University, in Bahir Dar, Ethiopia

Supervised by Dr. Nigus Gabbiye

Bahir Dar

JUN E, 2016

BAHR DAR UNIVERSITY INSTITUTE OF TECHNOLOGY

FACULTY OF CHEMICAL AND FOOD ENGINEERING

THE UNDER SIGNED HEREBY CERTIFIY THEY HAVE READ AND RECOMMEND TO THE FACULTY OF GRADUATE STUDY FOR ACCEPTANCE OF A THESIS ENTITILED ANAEROBIC CO-DIGESTION OF CAFTERIA LEFTOVER FOOD AND TOILET WASTES FOR BIOGAS PRODUCTION AND KINETIC EXPERIMENT :- BY KEFALE WAGAW YIZENGAW IN PARTIAL FULFILMENT OF THE REQUIRMENTS FOR THE DEGREE OF SCIENCE IN PROCESS ENGINEERING

DATE JUNE/2016

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TITLE: ANAEROBIC CO-DIGESTION OF CAFTERIA LEFTOVER FOOD AND TOILET WASTES AND KINETIC EXPERIMENT

FACULTY: CHEMICAL AND FOOD ENGINEERING

DEGREE: MSc CONVOCATION: JUNE YEAR 2016

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Nomenclature

Symbols and Abbreviations

A	Weight of dried residue +crucible
AD	Anaerobic digestion

ADM1	First anaerobic digestion model
B	Weight of crucible
BOD	Biological oxygen demand
BVS	Biodegradable volatile solids
C	Weight of wet sample+ crucible weight
C/N	Carbon to nitrogen ratio
COD	Chemical oxygen demand
D	Final (dry) weight of sample
DO	Dissolved oxygen
FAS	ferrous ammonium sulphate
HRT	Hydraulic retention time
HW	Human waste
K	equilibrium rate constant
Km	biomass degradation rate
LOF	leftover of food
M	morality of FAS
Q	FAS used in blank sample
rmax	initial microbes concentration
RVS	refractory volatile solids
VS	volatile solids
W	Initial (wet) weight of sample
WWTP	wastewater treatment plant

Acknowledgment

First of all I would like to thank GOD for giving me patience to accomplish my thesis work successfully. I am most grateful to my advisor Dr.Nigus Gabbye for advising and directing me throughout my thesis work.

I am grateful to Bahir Dar Institute of Technology, Bahir Dar University which provided scholarship for MSc study and for the financial support to this thesis.

It is my pleasure to thanks to my family and my wife Zemed workie for their parental love, support and care during my study. Special thanks to my brother Tamene wagaw for his support during thesis work.

Abstract

Anaerobic digestion is a process in which microorganisms break down biodegradable substrates in the absence of oxygen. It can be used to treat various organic wastes and recover bio-energy in the form of biogas, which contains mainly methane and carbon dioxide and the methane gas can be used for lighting and cooking. Primarily, the substrates physico-chemical properties (moisture content, ash content, total solid content, BOD and COD) were determined using standard methods. The result suggested that wot > pasta > Injera > bread > toilet waste in terms of biogas yield. In this work anaerobic digestion of cafeteria leftover food and toilet waste was carried out in a 5 L reactor (W/W

anaerobic digesters for a temperature range of 20-33^{0}C and initial pH of 4-9. During the experiments, the biogas production was recorded using water displacement method and by considering the ideal gas equation the concentration of methane was calculated. A maximum volume of 995.9ml was recorded at 30 day retention time at initial pH of 7 and at y ambient temperature condition. The maximum cumulative biogas production was 4001ml at 25^{0}C and 10:90 toilet wastes to cafeteria leftover food ratio. The kinetic parameters of the anaerobic digestion were investigated at selected temperatures The degradation rate constant was determined in temperature of 22, 28 and 33^{0}C. A pseudo first order kinetic model was proposed for the anaerobic digestion. From Arrhenius equation the obtained values of activation energy and pre-exponential factor was 7262.279 J/MOL and 717.408J/MOL respectively.

Key words: Co-digestion, Toilet waste, Cafeteria leftover food, Biogas, Kinetic model

CHAPTER ONE

1.0 INTRODUCTION

1.1 Anaerobic digestion

Anaerobic digestion is a process in which microorganisms break down biodegradable material in the absence of oxygen. Anaerobic digestion can be used to treat various organic wastes and recover bio-energy in the form of biogas, which contain mainly methane and carbon dioxide. Methane could be a source of renewable energy producing electricity in combined heat and power plants (Clemens et al, 2006).

Co-digestion is simultaneous digestion of homogenous mixture of two or more substrates. Traditionally anaerobic digestion was single substrate, single purpose treatment. Recently, it has been realized that anaerobic digestion as such become more stable when the verity of substrates applied at the same time is increased.

The most common situation is when a major amount of main basic substrates (e.g. manure of sewage sludge) is mixed and digested together with minor amounts of single or a verity of additional substrates (Braun,2002). The use of co-substrates usually improves the biogas yields from anaerobic digester due to positive synergisms established in the digestion medium and the supply of missing nutrients by the co-substrates (Mata-Alvarez et al, 2000).

Anaerobic digesters convert organic waste (agricultural and food waste, animal or human manure, and other organic waste) into energy (in the form of biogas). The benefits that the anaerobic digestion process provides are waste management, energy production, and fertilizer production. Anaerobic digestion can provide energy to those who do not already have it, or can produce clean energy as an alternative to carbon-intensive energy production. Energy provided to those who do not already have such as people living in rural area and those with different organic wastes enables them to accomplish more, and allows for a much higher quality of life. The fertilizer by-product is another benefit that can add value to an anaerobic digestion system.

Once a feedstock is consumed by the anaerobic digestion process, the leftover material can be used as a soil additive to enhance crop production. In rural settings, this fertilizer is best used locally or on-site of the anaerobic digester. Biogas which is produced from anaerobic digestion often has methane, carbon dioxide, hydrogen sulfide, ammonia, etc and the biogas can be used for lightning and cooking fuel and even for generator.

1.1.1 Biochemical process of anaerobic digestion

There are four major steps of anaerobic digestion as shown in the figure 1 and described in detail in the following section

Figure 1.1 the anaerobic digestion pathway

.1.1.1 Hydrolysis

The first step in the anaerobic digestion process, hydrolysis is the cleavage of chemical bonds by the addition of water. The digester feedstock may be made up of many different components and materials, and thus there are many different versions of hydrolysis; carbohydrates, fats, and proteins are all broken down into smaller molecules by this initial step of anaerobic digestion. In the case of a carbohydrate, polysaccharides (complex sugars) are broken down into monosaccharide, proteins are broken down into amino acids and lipids are degraded into fatty acids.

Figure 1.2 hydrolysis breaks down lactose, a polysaccharide, into galactose and glucose

In the case of lipids, usually triglycerides are split into three fatty acids and glycerol by the addition of three water molecules, as illustrated in figure 1.3.

Figure 1.3 hydrolysis of triglyceride result in glycerol and three fatty acid

In the case of protein peptide bonds are broken to separate amino acids

Figure 1.4 hydrolysis of protein involves breaking a peptide bond to separate amino acid

1.1.1.2 Acidogenesis

Acidogenic bacteria degrade the products of hydrolysis into volatile fatty acids. Some hydrogen, carbon dioxide, and acetic acid are also produced, which will skip the acidogenesis stage. Acidogeresis represents the portion of figure 1.5 in which bacteria produce acetate and butyrate (volatile fatty acids) from glucose.

Figure 1.5 During acidogenesis bacteria produce acetate and butyrate the fermentive pathway can also produce other by-products

1.1.1.3 Acetogenesis

In the third step of anaerobic digestion, Acidogenic bacteria consume precursors and produce acetate (acetic acid). One example of this process is the consumpiton of glucose, given in equation 1.1.

$$C_6H_{12}O_6 + 2H_2O = 2CH_3COOH + 2CO_2 + 4H_2 \text{----------} 1.1$$

1.1.1.4 Methanogenesis

The final step of anaerobic digestion is the formation of methane by bacteria called methanogens. For the most part, the biological process here is the breakdown of acetic acid, given in equation 2, though other forms of the reaction can also produce methane via anaerobic digestion.

$$CH_3COOH = CH_4 + CO_2 \text{----------} 1.2$$

1.2 Statement of the problem

Even though different higher institutions are planning to generate biogas from leftover food, the high organic acid nature of cafeteria leftover food substrate is supposed to lower the biogas productivity. This need to be addressed by using this substrate as a main substrate co-substrate with toilet wastes and formulating ratio at which better yield could be obtained is the first intention of this study.

At the same time, the biochemical digestion kinetics, which is important for biogas plant design, is not investigated for these specific substrate

1.3 Objective

1.3.1 General objective

The general objective of this work is the study of the co-digestion of anaerobic biogas production from cafeteria and toilet waste for design improvement.

1.3.2 Specific objectives

To determine physico-chemical properties of cafeteria leftover food and toilet wastes,

To investigate effects of operating conditions (temperature, initial pH and ratio of toilet wastes to cafeteria leftover food) for the anaerobic co-digestion on the yield of biogas,

To generate the reaction rate data and develop kinetic equation for biogas production from the anaerobic co-digestion process of these specific substrates

CHAPTER TWO

2.0. LITERATURE REVIEW

The International Water Association Anaerobic Digestion Model 1 (ADM1) is one of the most comprehensive anaerobic digestion models. The highly structured model includes multiple steps describing chemical and physical processes; it considers the four steps of hydrolysis, acidogenesis, acetogenesis, and methanogenesis, and how those steps differ for input carbohydrate, proteins, and lipids.

According to Kangle et al. (2012), anaerobic digestion is the most promising alternative to disposal of wastes, due to high energy recovery. The main objective of anaerobic digestion is the degradation and destruction of organic substances, with consequent reduction of the odorous emissions and pathogens. This conversion is catalyzed by a population of bacteria that operate in synergy, catalyzing different chemical reactions, hence the metabolic pathways involved in the anaerobic degradation are quite complex Hydrolysis is the rate-limiting step of the overall process degradation. In anaerobic digestion, co-digestion is the term used to describe the combined treatment of several wastes with complementary characteristics, being one of the main advantages of the anaerobic technology. Anaerobic digestion (AD) is a process by which microorganisms break down biodegradable material in the absence of oxygen. A great option for improving yields of anaerobic digestion of solid wastes is the co- digestion of multiple substrates. If co-substrates are used in anaerobic digestion system it improves the biogas yields due to positives synergisms established in the digestion medium and the supply of missing nutrients. Recent research on this topic is reviewed in the current paper. Special attention is paid to anaerobic co-digestion of animal waste, crop and crop residues, industrial sludge and municipal solid waste.

Researchers (Alemayehu et al, 2014) on evaluation of biogas production from cafeteria leftover food items was to generate biogas, an alternative and viable source of biogas for household consumption in particular from substrates consists of leftover food collected from Bahir dar university student cafeteria and cow dung as a co-substrate. They have done the experiment at varies reactor volumes with 60 day hydraulic retention time and they measured the amount of biogas by taking only one reactor water displacement method and they got 516 of biogas per one gram of substrate.

(Wu et al, 2013) developed a 3-D numerical simulation model based on conservation of mass, conservation of energy, and species transport that predicts biogas production from plug-flow anaerobic digesters. Their work uses a first-order kinetic model that considers the ratio of carbon, hydrogen, and oxygen of the feedstock.

Co-digestion of food waste and human excreta for biogas production by Dahunsi et al, (2013), the investigation of their work was design and construction of anaerobic digester from locally available raw material. By using this manufactured 40 liter anaerobic digester and 12kg of cafeteria leftover food and 3kg of toilet waste they produced 84,750 cm^3 of biogas this implies they produce 5.65ml biogas per gram of sample. They work on at ambient temperature by expecting it was under mesophlic condition (22°c-30.5°c). This work also investigates the population and species of microbes during anaerobic digestion, further they tried to investigate the distribution of micro organisms (Aerobes, Anaerobes, Fungi and Methanogens) during anaerobic digestion.

MSc thesis, (2014): Enhancement of the Performance of Existing Biogas Plant in Amhara Region (Debretabor Prison). The paper focuses on the enhancement of the performance of the existing biogas plant in Debra Tabor Prison by exploring the main difficulties. He observes in the prison, there are excess dry wastes, human execration as well as food waste. These wastes and excrete have the highest hydrocarbon composition, which can be converted to flammable organic component, to produce biogas. But these wastes and human excreta have environmental impact. Hence, biogas technology when properly utilized improves the sanitary and health conditions of the society. He investigated that the input substrate ratio is the main factor of biogas plant for well function

(Wu et al, 2013) also provides a review of many previous pieces of work. These include a model by Chen et al. that predicts gas production as a function of volatile solids, kinetic parameter, specific growth rate of bacteria, and temperature, but does not consider biochemical processes. Hill used this model and a computer analysis to determine maximum volumetric methane production, but did not use kinetics to model gas production over time. Other simple models address the effects of temperature, pH, nutrients, and toxins, but not kinetics of gas production based on biochemical reactions.

Complex models such as ADM1 and a model produced by Minott include as many as 34 differential and algebraic equations or consider spatial dependence and fluid dynamics. But during this thesis work it was develop a model which predicts the gas produced with time by lumping the intermediate process as one step reaction

2.1. Important operating parameters in AD process

The rate at which the microorganism grows is of paramount importance in AD process. The operating parameters of the digester must be controlled so as to enhance microbial activity and thus increase the anaerobic digestion efficiency of the system. Some of the parameters are discussed in the following section.

2.1.1. Waste composition/volatile solids

The wastes treated by AD may comprise a biodegradable organic fraction, a combustible and an inert fraction, the biodegradable organic fraction includes kitchen waste, food waste and garden wastes. The combustible fraction includes slowly degrading lignocelluloses organic matter containing coarser wood, paper, and cardboard as these lignocelluloses organic matter do not readily degrade under anaerobic condition they are better suited for waste to energy plants. Finally the inert fraction contains stones, glass, sand, metal, etc. This fraction ideally should be removed, recycled or used as land fill. The removal of inert fraction prior to digestion is important as otherwise it increases digester volume and wear of equipment. The volatile solid in organic waste is measured as total solids minus the ash content, as obtained by complete combustion of the feed. The volatile solids comprise the Biodegradable Volatile Solids (BVS) fraction and the Refractory Volatile Solids (RVS). It is seen that knowledge of the BVS fraction of substrate helps in better estimation of the biodegradability of waste. Lignin is a complex organic material that is not easily degraded by anaerobic bacteria and constitutes the refractory volatile solids (RVS) in organic matter. Waste characterized by high VS and low non-biodegradable matter are high potential for biogas production

2.1.2. Alkalinity

Acid neutralizing or buffering capacity of a digester is termed as alkalinity. It is attained with the help of number of substance and is mostly described by the carbonate, bicarbonate and hydroxide content of the digester (Chynoweth, 1987). Alkalinity in anaerobic digestion is also derived from the degradation of organic nitrogen containing compounds. Such compounds are amino acids and proteins.

During this degradation, amino groups are released which further lead to the production of ammonia which in its turnwill further react with carbon dioxide yielding alkalinity in the form of ammonium bicarbonate. According to speece et al. (1996) and Altamira et al, (2008) additional alkalinity can be generated from the metabolism of the microorganism in anaerobic digester. This type of alkalinity consists of the release of cations during the degradation of organic compounds.

2.1.3. Temperature

Temperature is a principal environmental factor affecting performance. It affects the physical and physico-chemical properties of compounds present in a digester and the kinetics and the thermodynamics of biological process (Boe, 2006). There are mainly two temperature ranges that provide optimum digestion conditions for the production of methane; namely mesophlic and thermophilic ranges. Mesophlic digestion takes place optimally around 30 to 38 ^{o}c or at the ambient temperatures between 20 to 45 ^{o}c. Thermophilic digestions takes place optimally around 49 ^{o}c to 57 ^{o}c or at elevated temperatures up to 70 ^{o}c (Boe, 2006).

2.1.4. Carbon to nitrogen ratio (C/N)

The relationship between the amount of carbon and nitrogen present in the feedstock is represented by the C/N ratio. It is very important process parameter of the process as a low ratio can cause ammonia inhibition where as high ratio will lead deficiency (Mata-Alvarez, 2000). The adjustment of the ratio to be within the optimum range (20-35) can be achieved through the co-digestion of different waste streams (Monnet, 2003). Optimum C/N ratio in anaerobic digester is between 20 and 30. A high C/N ratio is an indication of rapid consumption of nitrogen by methanogens and results in lower gas production. On the other hand lower C/N ratio cause ammonia accumulation and pH values exceeding 8.5, which is toxic to methanogenic bacteria.

2.1.5. Retention (or residence) time

Hydraulic retention time (HRT) and solid retention time (SRT) where HRT is the time that the fluid element of the feed remains in the digester. SRT is the time that refers to the residence of the bacteria (solids) in the reactor.

The required retention time of the completion of the AD reaction varies with differing technologies, process temperature, and waste composition. The retention time for waste treated in mesophlic digester ranges 10 to 40 days. Lower retention time is required in digester operated in thermophilic range. A high solid reactor operating in the thermophilic range has retention time of 14 to 30 days Jonathan (2014).

2.1.6. Mixing

The purpose of mixing in a digester is to blend the fresh material with digestate containing microbes. Also mixing prevents scum formation and avoids temperature gradients within the digester. However excessive mixing can disrupt the microbes so slow mixing is preferred. The type of equipment and the amount of mixing varies with the type of the reactor and the solid content in the digester.

2.1.7. Total solid content

Low solid anaerobic digestion system contains less than 10% solid content, medium solids content about 15-20% and high solids process range from 22% to 40%. An increase in total solids in the reactor results in the corresponding decrease in reactor volume

2.2. Kinetic Study of Anaerobic Co-digestion

Mathematical models can serve as useful tools to deepen the understanding of complex systems, and t facilitate operation and design of the process. If the behavior of a system can be predicted, the production can be optimized and process failure can be prevented. More effective processes could lead to a better competitiveness for biogas as an energy carrier. Despite of these motivations modeling has rarely been applied on anaerobic digestion. The obstacles for introducing modeling to the industry are amongothers that the models of anaerobic digestion are complex and require extensive input data, and that the performance of the models on full scale processes has not yet been tested (Batstone, et al., 2003)
Anaerobic digestion has traditionally been treated as a black box system due to the complexity of the process. To facilitate design, system analysis, operational analysis and control, a mathematical model describing the processes is required.

The different purposes require different ranges of accuracy and model complexity. A complex, non-linear model with focus on the biochemical reactions is well suited when the understanding of the process is important, e.g. for operational analysis or for research purposes. These models can facilitate optimization of operational stability and efficiency. When implementing model based control on a system, a linear and well parameterized model is needed with measurable key parameters as input signals. For design purposes, the model should focus on hydraulics and plant structure (Batstone, 2006).

In defining conversion, it was selected one of the reactants as the basis of calculation and then relates the other species involved in the reaction to this basis. In most instances it is best to choose the limiting reactant as the basis of calculation. It was developed stoichiometric relationships and design equations by considering the general reaction

$$a\,A + b\,B = c\,C + d\,D \qquad \text{----------2.1}$$

The uppercase letters represent chemical species and the lowercase letters represent stoichiometric coefficients. Taking species A as our basis of calculation, we divide the reaction expression through by the stoichiometric coefficient of species A, in order to arrange the reaction expression in the form

$$A + \frac{b}{a}B = \frac{c}{a}C + \frac{d}{a}D \qquad \text{----------2.2}$$

To put every quantity on a "per mole of A" basis, now we ask such questions as "How can we quantify how far a reaction has progressed?" "How many moles of C are formed for every mole of A consumed?" A convenient way to answer these questions is to define a parameter called conversion. The conversion X_A is the number of moles of A that have reacted per mole of A fed to the system.

X_A = Moles of A reacted/moles of A feed (H. Scott fogler)

From the experiment the limited reactant is the total volatile content of the feed substrate. From the digestion excess reactant was water.

The kinetic of biomass growth can be determined by measuring either substrate consumption or product (biogas) formation with time. Mathematical model was developed that describes biogas (methane) production with time.

CHAPTER THREE

3.0 MATERIAL AND METHOD

3.1 Materials

All chemicals used in this study are analytical grades, obtained from Faculty of Chemical and Food Engineering and Faculty of Civil and Water Resource Engineering at Bahir Dar Institute of Technology Bahir Dar University. pH standard solution were used (for buffer solution preparation during pH meter calibration) Sodium hydroxide (0.1M, for pH adjustment), hydrochloric acid (0.1M, pH adjustment), tap water (as raw material for anaerobic digestion). Potassium dichromate solution, silver sulphate, ferrous ammonium sulphate solution, Ferroin indicator and Liquid detergent were used to characterize the substrate and the slurry parameters such as to determine the COD of substrates.

3.2 Equipment

Plastic glucose bags (for biogas sample handling), DO meter (to measure the dissolved oxygen in the sample before and after incubation), BOD bottles (for sample handling for COD and BOD determination), incubator (to maintain the sample at dark condition), Oven (for moisture content determination maintain the sample at constant temperature), Furnace (for ash content determination maintain the sample at constant temperature), pH meter (to measure the pH of the substrate), Sample holding plastics, 20 liter plastic digester (for anaerobic co-digester), glass tube airtight with one side (for water displacement volume measurement setup preparation), 0.5 inch plastic pipe (for biogas transport from anaerobic co-digester to water displacement set up), glass jar (for volume measurement during buffer solution), 0.1M of sodium hydroxide and hydrochloric acid preparation), quartz paint container (for water displacement setup preparation for biogas volume determination) and safety clothes such as eye glass, glove, nose mask and cleaning agents such as soap.

3.3 Experimental Methods

3.3.1. Sample analysis

The physical and chemical properties of the feed stock were evaluated before and after digestion using standard methods (ASTM D2974). Parameters analyzed include total solid content, total solid volatile content, ash content, moisture content and also biological oxygen demand (Winkler method) and chemical oxygen demand (Open Reflux method).

3.3.1.2. Total solid and moisture content :

Total solid and moisture content the cafeteria leftover food and toilet waste were determined in a typical experiment as follows. The substrate was transferred to pre-weighed evaporating dish/crucible/ and weighed altogether using an electronic weighing balance and recorded. It was then dried at 105 ^{0}C in drying oven by measuring the weight of the sample with two hours time interval until the mass of the sample becomes constant. The expression for calculating moisture content on wet basis is written in equation 3.1

$$\text{Moisture (wet \%)} = \frac{\quad}{\quad} \times 100\% \quad \text{----------3.1}$$

The increase in the weight over that of empty dish represents the total solids. The solids of wet sample were calculated using the following equation.

$$\text{Total solid} = \frac{\quad}{\quad} \times 100\% \quad \text{----------3.2}$$

3.3.1.3. Total volatile and ash content :

The moisture removed sample was ignited at 550^{0}C for two hours in furnace, and then the sample was removed from the furnace, cooled in dissector and weighed. The remaining solid represents the ash content and total volatile solid content was determined as follows.

$$\text{Total volatile solid} = \text{total solid content} - \frac{\quad}{\quad} \times 100\% \quad \text{-----3.3}$$

3.3.1.4. The biochemical oxygen demand (BOD):

Oxygen content of the sample was determined using Winkler method (before and after incubation). The BOD level was computed using the initial and final (BOD5) concentration of dissolved oxygen. The BOD was determined by comparing the DO level of the sample that was incubated in a complete darkness at 20^{0}C for five days.

$$BOD_5[\quad] = (\text{initial DO} - DO_5) \times \text{dilution factor} \quad \text{---3.4}$$

$$\text{Dilution factor} = \frac{(\quad)}{\quad} \quad \text{---------- 3.5}$$

3.3.1.5. The chemical oxygen demand (COD) :

Organic and oxidizable inorganic substances in the sample were oxidized by potassium dichromate on 50% sulfuric acid solution at reflux temperature (150 ^{O}C). Sliver sulphate was used as a catalyst and mercuric sulphate was added to remove chloride interference. The excess dichromate was titrated with standard ferrous ammonium sulphate using orthophenanthroline ferrous complex as an indicator.

$$COD, mgO_2/ = (\quad)" \quad " \text{——} \quad \text{-----3.6}$$

$$\text{Molarity of FAS} \quad 0.04172 \quad 2 \quad 7, \text{————————} " \quad 0.25\text{--3.7}$$

3.3.2.Experiments

3.3.2.1. Investigating the effect of temperature and mixing ratio of toilet and cafeteria wastes

Randomized factorial design was used for the anaerobic digestion. Two factors such as temperature and waste ratio (toilet waste: cafeteria waste) with three level for temperature and five level for waste ratio were used to screen out the maximum biogas yield at a fixed amount of waste to water ratio, hydraulic retention time (1:1) and 30days retention time. The levels of waste ratio in percent were 0:100, 10:90, 30:70, and 50:50 90:10 and 100:0 and the levels of temperature were 20, and 25 ^{0}c and 35 ^{0}c. One experiment was done with replica of two. The mesophlic anaerobic digestion condition was selected. It was selected based on literature and its value is between 20 ^{0}c and 38 ^{0}c Kangle et al. (2012) and for this study anaerobic co-digestion condition mesophlic anaerobic digestion condition was selected because the actual ambient temperature in Ethiopia is within this range and also the anaerobic digesters which are already installed and the way of installing have no temperature controlling system.

3.3.2.2. Initial P H determination and adjustment of substrates

Initial pH of substrate was determined using pH meter. First the pH meter was calibrated at pH 4 and pH 7 using pH 4 and pH 7 buffer capsule. Then the pH meter was calibrated at this solution because from literature it was referred that the pH of the toilet waste is 4.52 (C.Guton; John, 2011) and left over food 6.01 (Alemayehu et al, 2014) that is why the instrument was calibrated at these pH so to determine the actual pH of the substrate. After determining the actual pH of the substrate sodium hydroxide and hydrochloric acid were used to increase and decrease the pH of the substrate respectively to the required value.

3.4. Result analysis method

3.4.1. Kinetic model of an anaerobic co digestion Process

Based on the experimental data, the volume of biogas (methane) at different time interval was recorded by water displacement method. From this data the conversion of methane was calculated using ideal gas equation. Second, the rate constants at three temperatures were determined by plotting $\ln([CH_4])$ versus time. Third, the pre-exponential factor and activation energy were obtained by plotting the logarithm of the rate constants (K') versus 1/temperature of absolute temperature using the Arrhenius equation.

3.5. Experimental procedures

3.5.1. Substrate collection and preparation

Subsrstrate as a feed for the digester was collected from Bahirdar Institute of Technology Student Cafeteria and from Dormitory toilets. The toilet waste was collected by diverting the toilet line from block No. 61 at sampling time in morning. The sample was collected by the expert who had good knowledge and experience about safety. At the end of diverged pipe there was a plastic sample collecting plastic material, which has sieve to pass the water and urine part through it.

After collecting enough amount of human waste it was transferred into the plastic handling equipment /baldy / and transported into the laboratories where the experiment was conducted. In the same way the cafeteria leftover food was collected by the same expert and sample was collected by considering the presence of all food items such as Injera, bread, cooked pasta, cooked rice and onion peels. The sample was taken during lunch time because at this meal time all food items are included at students menu.

Prior to the commencement of the experiment, the cafeteria leftover food was thoroughly homogenized manually to have particle size suitable for easy digestion and then mixed evenly with toilet wastes. The mixture used was a combination of cafeteria leftover food (0%, 10%, 30%, 50%, 90% and 100%) and toilet wastes (100%, 90%, 50%, 30%, 10% and 0%). This substrate was further mixed with water in a 1:1 m/v ratio to make final 4.3 liters slurry that was fed to anaerobic digester. The experiment was allowed run for thirty days.

3.5.2. Experimental setup and description for temperature and waste ratio investigation

After characterizing the substrate anaerobic digestion experiments with two replicas were performed in five liter cylindrical shape digesters. The experimental setup is presented in figure 3.1. The substrate was introduced into the reactor 15 cm lower than the full height to avoid over flooding. The digester has many components which are described on the figure.

Figure 3.1 Experimental setup of anaerobic co-digestion for temperature and waste ratio effect investigation

The anaerobic digestion was conducted in anaerobic digester in batch wise mechanism. Substrate was fed into the digester carefully by mixing with equivalent amount of water.

After the substrate was fed in to the digester it was homogenized using clean wooden material. Then porous non digestible plastic material was added in to the digester, because it is known that anaerobic digestion takes place due to the presence of microbes. Microbes inside the digester needed solid material with it and act accordingly. Increasing the exposed area between bacteria and substrate increase the activity of microbes

The digester cover was closed by insuring the absence of gas leakage by using sealants. Then ope safety valve to remove oxygen already present inside the digester for twenty four hours.

After a day, the valve closed because intermediate product of the digestion such as volatile material and others will develop and will escape. In the experimental setup there is another five liter cylindrical gas collector, which was filled by water and sealed the top cover by using sealants and checked whether there is water leakage or not at the bottom. The bottom valve opened through which the water is displaced when biogas developed /collected/ inside the collector. When the bottom valve opened there is no water leakage unless an external disturbance is applied /biogas developed and collected at the top layer of water inside the gas collector/ due to density difference. The biogas which is generated in the digester transfer to the gas collected cylinder with the glucose valve from the top of the digester to the bottom of the biogas collected cylinder.

Finally the temperature was set by pressing the upper and lower key by hand the set on temperature control board. The daily biogas amount generated was determined by reading the height difference on the glass collector cylinder. The volume daily produced biogas was determined and summed all the daily volumes for the thirty day retention time to get the total volume of biogas generated for on batch anaerobic digester from a specified amount of substrate.

Table 3.1: Experimental design on investigating the optimum temperature and waste ratio

Run	Temperature(Oc)	Ratio	Volume of biogas (ml)	Replica	Volume of biogas (ml)	Average biogas volume [ml]
1	20	10:90				
2	25	10:90				
3	33	10:90				
4	20	30:70				
5	25	30:70				
6	33	30:70				
7	20	50:50				
8	25	50:50				
9	33	50:50				
10	20	70:30				
11	25	70:30				
12	33	70:30				
13	20	90:10				
14	25	90:10				
15	33	90:10				
16	25	100:0				
17	25	0:100				

Ratio is based on toilet waste: leftover food

The experimental design in table 3.1 describes the type of factors and their level. For comparison of each substrate alone the biogas production was conducted at the same temperature (^{0}C) (25

3.5.3 Initial pH effect on biogas yield

3.5.3.1. Experimental setup and description

In this experimental work there were two basic setups: Anaerobic co-digestion setup and water displacement setup for biogas volume determination by using locally available materials.

Anaerobic co-digestion setup was prepared by taking 20 liter plastic digester which was bought from local market. The cover of the plastic digester was drilled by using hot metal rod with the diameter of the pipe, which is 0.5 inch and insert the pipe in the drilled hole with force and then it was airtighted using glue. Water displacement setup was prepared by using the materials which is listed in the material section.

The quartz paint container was collected from our institute store and the quartz paint container was drilled at the position 10 cm below from the top of it with the diameter of water discharged plastic pipe, 0.5 inch.

The quartz cover was drilled with glass tube diameter by using hot knife. Then added fill container with tap water up to the drilled position meanwhile the glass tube was fully filled with water.

The plastic pipe from the top of the plastic digester was inserted inside the water filled glass tube up to a random height. Finally it was checked by filling of water in the quartz paint container up to over flow position.

Figure 3.2 experimental setup of anaerobic digestion for initial pH effect determination

3.6. Result analysis procedures

3.6. Kinetic Model of Anaerobic Digestion

3.6.1 Basic Input-Output Kinetic Model Anaerobic Co-digestion

The purpose of this model is not to create entirely compressive model that takes all factors into account and predict biogas output to very high level of precision. However the models predict biogas output over time.

Figure 3.3 Basic input-output model of anaerobic batch reactor

3.6.2 Model assumptions

The initial assumptions of this model are given below

- Production of intermediate species is negligible (the reaction is a one step)
- The volume of anaerobic digester is constant, 5 liter.
- Ideal bacterial conditions
- Input substrate consist only C, H, N and O
- Products of reaction include only CO_2, CH_4 and NH_3

In the simplest case of a batch anaerobic digester, reactants fat, carbohydrate and protein are put into the digester in batch. Once in the digester, protein, fat and carbohydrate break down into products CO_2, CH_4 and NH_3 at a rate based on reaction coefficients.

Some of the input substrates don't break down all the way, and leave through the outlet. The amount that leaves instead of being broken down depends upon digester residence time of the feedstock and other parameters.

If the fractions of fat, protein and carbohydrates are known, the theoretical methane yield can be determined using the Buswell formula.

$$+ \quad " - " - + — \quad 2 \quad = - " - + - + — \quad 2 + - + - " - " — \quad 4 + NH3 \qquad 3.6$$

And also Hojlund Christensen investigated the average composition of organic compounds and is shown in table 3.2:

Table 3.2: Average composition of organic compounds

Compound	Elemental composition
Fat	$C_{57}H_{104}O_6$
Protein	$C_5H_7NO_2$
Carbohydrate	$C_6H_{10}O_5$

Assuming the input substrate to be a single compound by summing up the elemental composition of each compound, listed in table 3.2. So the input substrate has the molecular formula $C_{69}H_{121}O_{13}N$. Then

n" - " - + — =32.75 stoichiometry coefficient of water

- " - + - + — = 7.625 stoichiometry coefficient of carbon dioxide

- + - " - " —= 46 stoichiometry coefficient of methane

=1 stoichiometry coefficient of ammonia

Rewriting the reaction equation

$$C_{69}H_{121}O_{13}N + 32.75H_2O = 7.625CO_2 + 46CH_4 + NH_3 \text{---------} 3.7$$

This reaction equation is not balanced. The above reaction equation was further balanced by using general reaction equation balancing approach. The balanced reaction equation is given bellow:

$$C_{69}H_{121}O_{13}N + 33H_2O = 23CO_2 + 46CH_4 + NH_3 \text{----------} 3.8$$

The biochemical reaction is balanced and can be applied to any input with known relative ratios of carbon, hydrogen, oxygen and nitrogen. The model assumes that these elements are the only components of the feedstock.

Table 3.3: Balance of biochemical reaction used in this model

Components	Left	Right
Carbon	69	23+46=69
Hydrogen	121+66=187	46*4+3=187
Oxygen	13+33=46	23*2=46
Nitrogen	1	1

The rate law of the anaerobic digestion for forward reaction can be expressed by equation.

Based on the above assumptions

$$-r_{C_{69}H_{121}O_{13}N} = K[C_{69}H_{121}O_{13}N]^{n}[H_2O]^{P} \text{-----3.9}$$

Where $[C_{69}H_{121}O_{13}N]$ is the concentration of organic waste and $[H_2O]$ that of water, n is order of anaerobic digestion with respect to organic waste and p is order with respect to water and K is the equilibrium rate constant. However due to the high water to total volatile ratio, the change in water concentration can be considered as constant. Even if we used 1:1 (w/v) organic waste to water ratio, the average moisture content of the organic waste is 82.226% and the average volatile content of organic waste is around 17%. As a result the change in the concentration of water is almost constant. Hence, the reaction obeys pseudo first order kinetics. Finally the rate expression can be written as:

$$-r_{C_{69}H_{121}IO_{13}N} = \frac{[\quad]}{\quad} = K' \cdot [C_{69}H_{121}O_{13}N] \text{ ---------3.10}$$

where k' is modified equilibrium rate constant, $K' = K[H_2O]^{P}$.

The initial concentration of organic waste was determined based on the limited substrate which is total volatile content of organic waste. The initial concentration of organic waste at $t=t_0$, $[C_{69}H_{121}O_{13}N] = [(C_{69}H_{121}O_{13}N)_0]$ and at $t=t$, $[C_{69}H_{121}O_{13}N] = [(C_{69}H_{121}O_{13}N)_f]$. Then, the conversion of the organic waste ($X_{C69H121O13N}$) can be developed from mass balance as shown equation 3.11 below.

$$X_{C_{69}H_{121}IO_{13}N} = 1 - \frac{[(\quad)]}{[(\quad)]} \text{---------3.11}$$

From substitution of equation 3.11 in equation 3.10 and integration and rearrangement of equation 3.10 gives equation 3.12.

$$-\ln(1 - X_{C_{69}H_{121}IO_{13}N}) = \text{" " " " " " " } 3.12$$

$$K_2 = \text{" } \overline{\text{"}} \text{ " " " " " " " " " " " " " " " " " " " } 3.13$$

The concentration of the product/ substrate can be calculated from ideal gas equation as shown in equation 3.14 and 3.15.

$$XC_{69}H_{121}IO_{13}N = 1" \frac{\quad}{"\ "} " " " " " " " " " 3.14$$

Daily partial pressure of biogas (methane) was calculated by using equation 3.15 by taking literature value density, 0.93 gm/m^3, methane density 0.656 kg/m^3, carbon dioxide density 1.977 kg/m^3 and ammonia density 0.73 kg/m^3 at 25^{O}C (Basic Data on Biogas, 2nd edition, Sweden, 2012) biogas and daily height lowered in gas collector cylinder.

Partial pressure of methane = density of methane " ! ! " " " " " 3.15

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Substrate Characterization

Substrates for the experiment were obtained from Student cafeteria and Student dormitory toilets. All samples prepared were determined for their physico-chemical properties before charged into the anaerobic bio-digester. A simple kinetic model with lamped parameters was developed and fitted with experimental results.

Types of leftover meal in the cafeteria considered in this study are: Injera, bread, cooked pasta, cooked rice, onion peels and marmalade. The composition of leftover food from student cafeteria is presented in table 4.1.

Table 4.1: Components present in cafeteria leftover food

Component	Composition (%)
Injera	50
Bread	20
Cooked pasta	13.6
Cooked rice	12
Onion peels	3.5
Marmalade	0.9

4.1.1 Moisture content

The moisture content of the substrates obtained follow the protocol stated in section 3.3.1.2 presented in table 4.1. As it can be seen in the table, bread has the highest moisture content while toilet waste has the lowest moisture content. From our input substrates relatively the highest biogas yield can be achieved from toilet waste substrates due to its high total solid content. It is known that substrates which are used as a biogas source should have enough amount of biodegradable biomass, high solid content implies relatively much amount of biodegradable content of substrate.

Table 4.1 Moisture content of wastes

Sample		Sample mass (gram)	Moisture content (%)
Cafeteria wastes	Bread	68.60	41.23
	Injera	64.51	38.60
	wot	6.58	72.810
	Pasta	32.31	33.86
Toilet waste		11.57	24.63

So substrate with high total solid content has high content of the acetic acid sourced as a result the substrates can be priorities on their biogas potential as follow toilet wastes > Pasta > Injera > bread > watt.

But further ultimate analysis such as volatile content determination is needed to strictly predict the biogas potential from the total solid content of substrate, because from this fraction of total solid content digestible matter will be small.

4.1.2 Volatile solid content

For the determination of the volatile solid content of the substrate pre-dried of substrate sample was burned in a furnace at 550^{o}C for two hours. The mass of the ash was measured using digital balance with precision of two decimal places. The entire volatile solid content is assumed to escaped by this two hours burning and the escaped percentage of mass represents the volatile solid content determined by subtracting the ash content from total solid content of the sample.

Table 4.2: Volatile content of different wastes

Sample		Sample mass (g)	Total volatile Content (%)
Cafeteria wastes	Bread	40.32	13.25
	Injera	39.61	18.08
	wot	1.79	31.41
	Pasta	21.37	20.27
Toilet waste		8.72	2.51

The composition of the substrates interms of total volatile content is presented in table 4.2. As it can be seen wot has high total volatile content; while toilet waste has low total volatile content. Since total volatile content represents the biodegradable component of the sample during anaerobic digestion, we can arrange the substrates based their biogas potential. It can be arranged based on their biogas producing potential watt > pasta > Injera > bread > toilet waste.

All compounds are decomposed to simple soluble molecules and all intermediate products such as alcohols, carbonic acid, and volatile fatty acids produced at acids produced at acidogenesis stage of anaerobic digestion is from volatile content of the substrate.

4.1.3 BOD and COD of substrates

Table 4.3 BOD and COD of the substrate used for biogas production

No.	HW to LOF Ratio	BOD [mg/l]	Literature value [mg/	COD (mg/l)	Literature value [mg/l]
1	100:0	38	37-434	2590	610-18,550
2	90:10	45	>>	2350	>>
3	10:90	43	>>	3500	>>
4	50:50	35	>>	3150	>>
5	0:100	41	>>	3750	>>

Ratio is based on toilet waste: leftover food

Source: for literature values J.Natan.sci.Coun.Sri Lanka, 1993

Similarly the BOD and COD of the substrates at fed ratios were measured and presented in table 4.3. As it is seen in the table the value of the BOD and COD seems no direct relationship with the waste ratios. This implies both wastes have nearly similar biological oxygen demand. When cafeteria leftover food and human waste compared with industrial wastes the value of BOD is small, this implies that sample has low amount of microbes. The values of COD are moderate when it is compared with industrial wastes.

4.2. Effect of operation conditions on biogas yield

Table 4.4 Effect of temperature and feed ratio on biogas yield at retention time of 30 days

Run	Temperature(^{o}C)	Ratio	Volume of biogas (ml)	Replica Volume of biogas (ml)	Average biogas volume [ml]
1	25	0:100	5628..12	4982.52	5305.35
2	20	10:90	1932.16	1901.97	1917.06
3	25	10 :90	4017.54	3985.08	4001.00
4	33	10:90	2226.43	2161.75	2194.09
5	20	30 :70	1546.64	1718.00	1632.32
6	25	30: 70	3687.28	3345.00	3516.14
7	33	30:70	1028.92	987.80	1008.36
8	20	50:50	1328.36	1513.36	1420.86
9	25	50:50	3486.94	3396.38	3441.66
10	33	50 :50	3351.09	2467.95	2909.52
11	20	70:30	2118.62	1938.26	2028.44
12	25	70:30	2113.43	3783.62	2948.53
13	33	70 :30	1028.92	987.82	1008.37
14	20	90 :10	966.08	966.88	966.44
15	25	90:10	3392.75	2177.41	2785.08
16	33	90:10	2245.425	1343.455	1794.44
17	25	100:0	2118.62	1938.26	2028.44

Ratio is based on toilet waste: cafeteria leftover food

The effect of temperature on the yield of biogas at different substrate ratios was presented in table 4.4. As it is can be seen in table 4.4, the cumulative biogas produced at specified temperatures from each ratio is highest at 25^{o}C. From the table it can be also notice that the ratio of toilet to cafeteria leftover food has a maximum biogas yield at thirty day retention time.

The maximum average volume of biogas produced at 25^{o}C, 10: 90 toilet to cafeteria leftover food ratio for thirty day retention time from 2.15kg solid waste is 4001ml. The experiment from only cafeteria a

toilet waste was conducted at 25 °C for comparison of the biogas potential and it was observed from the figure that the cumulative biogas volume from cafeteria leftover food is higher than the toilet waste alone

4.2.1 Effect of temperature on daily biogas yield

Figure 4.1. The effect of temperature on biogas yield at 10:90 (toilet to cafeteria)

The effect of temperature on daily biogas yield was investigated on three different temperatures in mesophlic digestion conditions and at optimum substrate ratio of thirty day retention time. The yield of biogas is presented in figure 4.1. As it can be seen in the figure; the anaerobic digestion is strongly dependent on temperature. At 20 °C, the yield of biogas was lower and as the temperature increase from 20 °C to 25 °C the biogas yield is increased from 1917.065 to 4001 ml. This implies that the kinetics and thermodynamics of microorganisms inside the digester is very much sensitive to temperature. The cumulative biogas yields from 10:90(m/m) of toilet and cafeteria wastes are 1917.065 ml, 4001ml, and 1194.088ml at 20 °C, 25oC and 33 °C respectively.

4.2.2. Effect of Substrate Ratio on Daily Biogas Yield

Figure 4.2 Effect of substrate ratio on biogas yield at t = 25^{O}C

The effect of substrate ratios on daily biogas yield was investigated for a wide range of substrate ratios in wet base at a temperature of 25^{O}C and retention time of thirty day. As it can be seen in figure 4.2 anaerobic digestion is strongly dependent on the amount of cafeteria leftover food in the sample. As the amount of cafeteria leftover food with toilet waste increase, the yield of biogas production increase. This is due to the low total volatile content of toilet wastes when compared with cafeteria leftover food (see table 4.2). The average cumulative biogas yield at 25^{O}C for thirty day retention time is 2028.44ml, 2785.0785ml, 3441.66ml, 3516.66ml, 4001ml, and 5305.l35ml for the range of substrate ration of (toilet waste to cafeteria leftover food) 100:0, 90:10, 50:50, 30:70, 10:90 and 0:100 respectively

4.2.3. Effect of Initial pH on Daily Biogas Yield

Figure 4.3 Effect of initial pH on biogas production at 10:90 waste ratio and t= 25°C

The daily biogas produced from organic fraction of toilet and cafeteria waste for different solution pH, at ambient temperature was presented in figure 4.3. It is noted that the biogas production of toilet and cafeteria wastes was performed without inoculums effect. The production is maintained for about 30 days. Interestingly it was observed that the biogas production starts at different for each pH treatment. As it can be seen the production starts after nine days for pH = 4 treated substrate, after fifteen days for pH=9 treated substrate and after four days for pH=7 treated substrate. This is in agreement with results reported by Vedrenne et al, 2005 at similar solution pH of 4, 5.5 6, 7 and 9. This demonstrates that the initial pH of the substrate is deliberately changes the activity of microorganism is retarded, because the population of bacteria was affected that is why the yield of biogas decreased. As seen from figure 4.3 the lag time at each pH indicates the effect of pH on microbe's population growth and activity. It is also clearly seen that the higher the pH the shorter is the reaction time to complete the reaction. If the acidity or basicity of substrate is far from optimum value they take much time for adaption and start their digestion activity. After digestion the pH of the slurry was 6.02, 7.23 and 7.62 for initial pH of 4, 7 and 9 respectively. This means that there was a buffering mechanism of pH made the environment favorable to digestion.

The final volumes of biogas from 2.15 kilogram of cafeteria and toilet wastes are 995.9 mL, 694.14 mL 256.49 mL corresponding to the reaction condition of pH = 7, pH = 4 and pH = 9 respectively. This suggested that pH 7 is an appropriate start up condition for anaerobic digestion of leftover cafeteria and toilet waste.

4.2.4 Significance test for correlation

Table 4.5 Tests of Between-Subjects Effects

Dependent Variable: volume					
Source	Type III Sum of Squares	Df	Mean Square	F	Sig.
Corrected Model	26100895.836[a]	14	1864349.703	8.886	.000
Intercept	152327176.566	1	152327176.566	726.015	.000
Temp	17941888.299	2	8970944.149	42.757	.000
Sub	2409975.252	4	602493.813	2.872	.060
temp * sub	5749032.285	8	718629.036	3.425	.019
Error	3147191.928	15	209812.795		
Total	181575264.329	30			
Corrected Total	29248087.763	29			

a. R Squared = .892 (Adjusted R Squared = .792)

The significance of temperature and substrate ratio was presented in table 4.5, which is the output of SPSS version 20. From the significance value we can see both temperature and the interaction of substrate ratio and temperature are significant at 5% while substrate ratio is significant at 6% level.

Table 4.6 multiple comparison of temperatures

Dependent Variable: volume Scheffe						
(I) temperature	(J) temperature	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
20	25	-1745.5097*	204.84765	.000	-2301.4226	-1189.5968
	33	-235.4322	204.84765	.531	-791.3451	320.4807
25	20	1745.5097*	204.84765	.000	1189.5968	2301.4226
	33	1510.0775*	204.84765	.000	954.1646	2065.9904
33	20	235.4322	204.84765	.531	-320.4807	791.3451
	25	-1510.0775*	204.84765	.000	-2065.9904	-954.1646

Based on observed means.

The error term is Mean Square(Error) = 209812.795.

*. The mean difference is significant at the .05 level

The digester operating temperature has a significance effect on the yield of biogas. As presented in table 4.6, when the digestion temperature increase from 20 to 25 ^{O}C the mean difference of biogas volume is significant at 0.05 level while working the reaction at 33 ^{O}C rather than 20 ^{O}C the mean difference of biogas production is not significance. Generally increasing the reaction temperature from 20-25 ^{O}C and decreasing from 33-25 ^{O}C the mean difference of the biogas production is significant at 0.05 level.

Table 4.7 Multiple Comparisons of substrate ratios

Dependent Variable: volume

Scheffe

(I) substrate ratio	(J) substrate ratio	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
10:90	30:70	-93.9688	264.45718	.998	-1018.5208	830.5832
	50:50	-221.5247	264.45718	.948	-1146.0767	703.0273
	70:30	374.0428	264.45718	.736	-550.5092	1298.5948
	90:10	520.4883	264.45718	.453	-404.0637	1445.0403
30:70	10:90	93.9688	264.45718	.998	-830.5832	1018.5208
	50:50	-127.5558	264.45718	.993	-1052.1078	796.9962
	70:30	468.0117	264.45718	.554	-456.5403	1392.5637
	90:10	614.4572	264.45718	.298	-310.0948	1539.0092
50:50	10:90	221.5247	264.45718	.948	-703.0273	1146.0767
	30:70	127.5558	264.45718	.993	-796.9962	1052.1078
	70:30	595.5675	264.45718	.326	-328.9845	1520.1195
	90:10	742.0130	264.45718	.151	-182.5390	1666.5650
70:30	10:90	-374.0428	264.45718	.736	-1298.5948	550.5092
	30:70	-468.0117	264.45718	.554	-1392.5637	456.5403
	50:50	-595.5675	264.45718	.326	-1520.1195	328.9845
	90:10	146.4455	264.45718	.988	-778.1065	1070.9975
90:10	10:90	-520.4883	264.45718	.453	-1445.0403	404.0637
	30:70	-614.4572	264.45718	.298	-1539.0092	310.0948
	50:50	-742.0130	264.45718	.151	-1666.5650	182.5390
	70:30	-146.4455	264.45718	.988	-1070.9975	778.1065

Based on observed means.

The error term is Mean Square(Error) = 209812.795.

As in table 4.7 presents increasing the amount of toilet waste or decreasing the amount of cafeteria leftover food in the sample has no significant effect on the mean differences of biogas production at 0.05 levels. But as seen in the table the mean difference of biogas volume at much amount of cafeteria leftover food and low amount of the toilet waste becomes significant. Generally the substrate ratio has relatively has less significant effect than temperature on biogas volume.

4.3. Determination of Kinetic Parameters

In this work the kinetic data was collected by volume measurement of the daily biogas volume using water displacement method, which can provide real time monitoring of the reaction. The biogas volume difference gives an indication of the conversion of volatile content fraction of organic compound into methane, carbon dioxide and ammonia.

The conversion X (%) of methane used in this work was monitored by measuring the volume of biogas at the specified time and varies temperatures based on ideal gas equation and the result of kinetic parameters was reported as follows.

4.3.1 Rate Constant, Activation Energy and Pre-exponential Factor Determination

It was considered that the digestion is occurred in liquid phase and it is supposed microbes are used to initiate the digestion for the formation of methane during the course of reaction. Table 4.5 represents the fractional conversion of volatile content fraction of organic compounds in digestion time of 30 days. The digestion temperatures were 20, 25 and 33 ^{O}C. Those temperatures were selected since the reaction condition is mesophlic and from section 2.2.2 mesophlic temperature range is 20-38 ^{O}c. The lower temperature level was selected to see the effect of temperature at this minimum temperature of the mesospheric digestion condition. On one hand the upper level of temperature 33 ^{O}C is limited to the maximum temperature Bahir dar city found. This is to predict the biogas yield that we can get from installed digesters around the city since they have no temperature control mechanism with their design

The value of rate constant was determined from the plot of ln (1 – X $_{me}$) versus time. The result is presented in figure 4.5 As it can be seen the plot yields a straight line with correlation coefficient from 0.932-0.964 for the three (20, 25, 33 ^{O}C) temperatures considered in this work. The reaction rate constant (K•) with a lamp parameter model is obtained from the slop of plot ln (1 – X $_{me}$) versus time. The values are found to be 0.0029-0.0409 day^{-1} for the range of temperature considered. This suggests that first order kinetics can be used to describe methane generation of cafeteria leftover food and toilet waste (figure 4.5). The rate constants at each temperature and their corresponding correlation coefficient are listed in table 4.6. The rate constants represent the measure of the degradation rate. The higher rate constant value implies the higher the biodegradability of the digester.

Table 4.8 Methane formation conversion at temperatures 20, 25, and 33 °C

Digestion time	X_{me}			-ln(1-X_{me})		
	20 °C	25 °C	33 °C	20 °C	25 °C	33 °C
0	0	0	0	0	0	0
2	0.10	0.161	0.012	0.105	0.176	0.012
6	0.17	0.371	0.0304	0.186	0.463	0.0308
8	0.246	0.458	0.0456	0.282	0.613	0.0466
12	0.271	0.539	0.0517	0.316	0.774	0.053
16	0.298	0.565	0.0608	0.353	0.832	0.0627
18	0.344	0.607	0.064	0.422	0.934	0.066
24	0.362	0.677	0.07	0.449	1.13	0.0725
26	0.377	0.697	0.0822	0.473	1.19	0.0858
28	0.393	0.72	0.085	0.499	1.27	0.0888
30	0.407	0.739	0.0914	0.523	1.34	0.0958

Table 4.9 Reaction rate constants at the given temperature

Temperature (K)	K (1/day)	R^2
293	0.0159	0.932
298	0.0409	0.964
306	0.0029	0.941

Figure 4.4 plots of -ln (1-Xme) versus time [day]

4.3.1.1. Michaelis–Menten model

Even though there are many chemical and physical reaction takes place in anaerobic digestion process, in four most important steps for biogas production many intermediate products due to biochemical transformation reaction. But here the whole system is lumped to one step reaction as described in the above sections. In section 4.3.1.1 it was tried to investigate and develop the model and validate the model by experimental data generated from the laboratory.

Further we fit the experimental results with Michaelis-Menten equations and the relation of microbial population with methane product was investigated. Michaelis-Menten developed that the rate of product formation is proportional to microbial growth.

$$= \frac{}{} = " \frac{}{+} " \ " \ " \ " \ " \ " \ " \quad 4.3$$

The values of kinetic parameters were estimated by conducting experiment and generating concentration–time data. The reaction rate data for the corresponding concentration–time data was generated by differentiated concentration–time data by using numerical methods. This method was used because of the data points in the independent variable is equally spaced. The result plotted graphically as shown at figure 4.5, so that the validity of kinetic model was tested and kinetic parameters were estimated.

As it is shown in figure 4.6 the value of rate constant was determined from the plot of [CH4]/Reaction rate versus [CH4] plotting yield straight line equations with goodness of fit (correlation coefficient) ranging from 0.932-0.964 at different temperatures with slope (K_m) ranges 0.667-1.601 day^{-1}.

This figure shows that first order kinetics can be used to describe methane generation of cafeteria leftover food and toilet waste (figure 4.5). The rate constants at each temperature range from 0.08-1.565 and their corresponding correlation coefficient are 0.928-0.993 listed in table 4.7 The rate constants represent the measure of biodegradation rate. The higher of rate constant value, the higher the biodegradability of the digester. We can see in the table the degradation rate of substrates is highly depending on temperature. The interaction of microbe with substrate is higher at 25 ^{o}C when compared to at 33 ^{o}C. And the initial concentration of microbes in was also following the same trend as substrate microbe•s interaction rate.

Table 4.10 kinetic constants and correlation coefficients

Kinetic model	Temperature (^{o}C)	Reaction rate constants	Correlation coefficients
Michaelis€ menten model	20oc	rmax=0.15,km=1.106	0.937
	25oc	rmax=1.565,km=1.601	0.929
	33oc	rmax=0.08,km=0.667	0.993

Figure 4.5 formation of methane vs.biodegradtion rate with methane concentration using Monod model

The activation energy for the anaerobic digestion reaction was calculated using Arrhenius equation 3.12 from the reaction rate constants shown in table 4.6. As it is shown in figure 4.6 the correlation coefficient (R^2) 0.993 indicates a good linearity between lnK' and 1/T in the temperature range of 20 33^{o}C. The value of activation energy and pre-exponential factor from figure 4.7 was 72262.279 J/ MOL and 717.408 J/MOL respectively. Therefore, the Arrhenius equation for the reaction rate and the reaction temperature (20-33^{o}C) could be written as equation 4.1 and substituting the slope and the intercept it can be written as equation 4.2.

$$K = \text{—} \quad \text{"k} \quad \ln K = \ln A \; \frac{E}{R\,T} \text{"} \quad \text{"} \quad \text{"} \quad \text{"} \quad 4.1$$

$$\ln K = 8.6\,4\,\text{"}3 \quad 8\,7\,3\,5\,\text{"} \; \frac{1}{T} \text{"} \quad \text{"} \quad \text{"} \quad \text{"} \quad \text{"} \quad \text{"} \quad 4.2$$

The activation energy for the anaerobic digestion of diluted labaneh whey for biogas production with temperature range (32-37°C) was 5242.333 J/MOL [29].

Figure 4.6 plots of lnK• versus 1/T for anaerobic co-digestion

In this work, the activation energy obtained for the anaerobic co-digestion was higher than the value listed in the literature (Vedrenne et al, 2005).

CHAPTER FIVE

5.0. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

Biogas production from cafeteria leftover food and toilet waste was studied in 5 liter anaerobic digester. The substrates used as an input for the experiment were categorized and prioritized according to their total volatile content for biogas yield potential as: watt > pasta > Injera > bread > toilet waste. This is based on the total volatile content.

The value of the digestion parameters: Cafeteria leftover food to toilet waste ratio 1:9 and digestion temperature 25^{o}C for 30 day digestion retention time was investigated to give the maximum conversion 74 % within the given range of parameters. According to this study the highest amount of biogas (4.001 liter) was produced from 0.215kg of toilet waste and 1.95 kg of cafeteria leftover.

The kinetic parameters were determined by generating the conversion of methane at different reaction conditions from the volume of biogas generated. Temperatures: 20, 25, and 35^{o}C were used to study the temperature dependency of rate constants hence constants were determined at each temperature. The values of activation energy and pre-exponential factor were determined by fitting the reaction rate constants at different temperatures in Arrhenius equation. From Arrhenius equation the obtained values of activation energy and pre-exponential factor were 7262.279 J/MOL and 717.408J/MOL respectively Then it was found that a pseudo first order kinetic model was proposed for anaerobic co-digestion of cafeteria and toilet wastes.

5.2. Recommendations

This thesis work investigates the possibility of employing volume measurement method of monitoring digestion progress for anaerobic co-digestion reaction. According to all the results and observations, the key findings in this thesis led to the following ideas for further considerations:

1. Although the pseudo first order reaction kinetics was proposed by monitoring the methane concentration by volume measurement and methane concentration using ideal gas equation, study the methane concentration profile for the digestion progress using biogas analyzer leads to the general understanding.
2. The temperature effect at thermophilic anaerobic condition should be done to compare the yield and biogas quality.
3. The effect of digestion retention time on biogas yield should be done further beyond 30 days.

Appendix

TableAPP.1: Concentration of substrate and product at temperature of 25

Tableapp2: Concentration of substrate and product with time at temperature of 20

TableAPP.3: Concentration of substrate and product with time at temperature of 33

Table APP 4 90% toilet waste: 10% leftover food [20°c]

Date	Level[ml]	Volume of biogas[ml]
07/02/07	322	12.568
08	315	10.997
09	302	4.713
11	298	6.284
17	295	4.713
19	288	12568.
22	286	5683.142
23	283	4.713
24	282	1.571
25	279	6.284
26	274	7.855
29	273	1.571
30	268	7.885
02	266	3.142

Waste to water ratio= one

TableAPP.5:10% toilet waste and 90% leftover food [20°c]

Date	Level [ml]	Biogas volume [ml]
7/02/07	329	1.571
8	312	26.707
11	306	9.426
17	266	62.84
19	264	15.71
22	243	17.281
23	238	7.855
24	233	7.885
25	229	6.284
26	223	9.426
29	216	10.997
30	214	3.142
02	206	12.568
03	202	6.284

Waste to water ratio= one

TableAPP.6: 50%toilet waste: 50% leftover food [20]

date	Level [ml]	Volume of biogas [ml]
7/02/07	323	10.997
8	315	12.568
11	313	3.142
17	309	6.284
19	307	3.142
22	306	1.571
23	304	3.142
24	303	1.571
25	302	0
26	299	1.571
29	298	4.713
30	298	1.571
02	296	3.142
03	296	0

Waste to water ratio= one

TableAPP.7: 50%toilet waste: 50% leftover food [36]

Date	Level[ml]	Volume of biogas produced [ml]
7/02/07	329	1.571
8	204	196.375
11	184	31.42
17	164	31.42
19	156	12.568
22	150	9.426
23	145	7.855
24	143	3.142
25	139	6.284
26	133	9.426
29	126	10.997
30	122	3.142
02	118	6.284
03	108	15.71

Waste to water ratio= one

TableAPP.8: 50% toilet waste: 50% leftover food [25°c]

Date	Level [ml]	Volume of biogas produced [ml]
25/03/07	299	48.701
26	277	34.562
28	244	51.843
29	229	23.565
01	204	39.275
02	193	17.281
03	179	21.994
05	165	21.994
06	157	12.568
07	153	6.284
08	145	12.568
10	137	12.568
12	126	17.281
13	124	3.142
15	119	7.855

Waste to water ratio= one

TableAPP.9: 90% toilet waste:10% leftover food [13°c]

Date	Level [ml]	Volume of biogas produce [ml]
25/11/07	286	69.124
26	244	65.982
28	218	40.846
29	210	12.568
01	198	18.852
02	192	9.426
03	184	12.568
05	178	9.426
06	170	12.568
07	170	0
08	165	7.855
10	161	6.284
12	152	14.139
13	149	4.713
15	144	7.855

Waste to water ratio= one

TableAPP.10 90% toilet waste: 10% leftover food [33°c]

Date	Level [ml]	Volume of biogas produce [ml]
25/03/07	329	1.571
26	323	9.426
28	320	4.713
29	318	3.142
01	311	10.997
02	306	7.855
03	302	6.284
05	291	17.281
06	289	4.713
07	286	4.713
08	270	25.136
10	252	34.562
12	241	14.139

Waste to water ratio= one

TableAPP.11 50% toilet waste 50% leftover food [33°c]

Date	Level [ml]	Volume of biogas produce [ml]
25/03/07	326	6.284
26	320	9.426
28	315	7.855
29	313	3.142
01	310	4.713
02	310	0
03	308	3.142
05	306	3.142
06	302	6.284
07	301	1.571
08	299	3.142

Waste to water ratio= one

TableAPP.12: 50% toiletwaste:50% leftover food [25°c]

Date	Level [ml]	Volume of biogas produce [ml]
07/01/07	206	197.804
08	198	12.568
9	188	15.71
13	169	17.281
15	150	29.349
19	136	21.994
21	130	9.426
23	123	10.997
24	121	3.142
25	118	4.713
26	114	6.284
29	107	10.997
01	105	3.142
03	105	0

Waste to water ratio= one

TableAPP.13:10% toilet waste: 90% leftover food [33°c]

Date	Level [ml]	Volume of biogas produce [ml]
07/01/07	329	1.571
08	327	3.142
9	326	1.571
13	325	1.571
15	324	1.571
19	322	3.142
21	321	1.571
23	320	1.571
24	319	1.571
25	316	4.713
26	315	1.571

Waste to water ratio= one

TableAPP.14 90% toilet waste: 10% leftover food [25°c]

Date	Level [ml]	Volume of biogas produce [ml]
07/01/07	325	7.855
08	324	1.571
9	318	9.246
13	316	3.142
15	307	14.139
19	303	6.284
21	300	4.713
23	298	3.142
24	294	6.284
25	289	7.855
26	285	6.284
29	283	3.142
01	281	3.142
03	268	20.423
04	252	25.136

Waste to water ratio= one

TableAPP.15 10% toilet waste: 90% leftover food [20°c]

Date	Level [ml]	Volume of biogas produce [ml]
07/01/07	296	53.414
08	275	32.991
9	257	40.846
13	247	12.568
15	240	14.139
19	225	23.565
21	219	9.426
23	214	7.855
24	209	7.855
25	204	7.855

Waste to water ratio= one

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