ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

MASTER OF SCIENCE IN CHEMICAL ENGINEERING
(ENVIRONMENTAL ENGINEERING STREAM)

Biogas Production from Mixture of Water Hyacinth and Tannery Flesh Waste Using Inoculum from Cow Dung

---

By: Wondmeneh Hadgu

A thesis is submitted to Graduate department of Addis Ababa University in partial fulfillment of the degree of Master of Science in Chemical Engineering under Environmental Engineering stream

Advisor: Dr. Anuradha Jabasingh

December, 2021
Addis Ababa Ethiopia

ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

MASTER OF SCIENSE IN CHEMICAL ENGINEERING

(ENVIRONMENTAL ENGINEERING STREAM)

This research paper titled “Biogas Production from Anaerobic Digestion of Water Hyacinth and Tannery Flesh Waste Using Inoculum from Cow Dung” was submitted to graduate program of Addis Ababa University for partial fulfillment for requirement of degree in Master of Chemical Engineering under Environmental Engineering stream. And approved by:

	Date	signature
Advisor		
Dr. Anuradha Jabasingh:	…………………….	………………….
Internal Examiner		
External examiner		
School Dean		
Dr. Abubeker Yimam	……………………...	…………………….

Declaration

This research thesis titled ‘Biogas Production from Anaerobic Digestion of Water Hyacinth and Tannery Flesh Waste Using Inoculum from Cow Dung’ is my original work and not presented by other person for award of degree or research projects in this University and others and all resource and material used for this research have been acknowledged. And it is undersigned declared by:

Wondmeneh Hadgu
Date ………………………… Signature …………………………….

Abstract

Disposal of untreated tannery wastes into land and water bodies results in water pollution and air pollution which in turn leads to greenhouse gases. With increased emphasis on climate change mitigation, waste management and, re-use of waste as a resource new environment friendly technological approach such as anaerobic digestion has received increased attention. This research presents the experimental results of anaerobic digestion of tannery solid waste and water hyacinth in different proportions. Four bench scale anaerobic digesters with different feedstock composition of 100%, 75gram:25gram, 50gram:50gram, and 25gram:75gram (Tannery solid waste to Water hyacinth) have been used in the experiment. The retention time of the experiment ranged 82 days for the digester containing 75gram Tannery solid waste and 25gram Water Hyacinth at ambient temperature of 37°C and pH of 7. Estimation of biogas produced and its quality was determined by the water displacement method using the biogas analyzer for each digester. It was found that, the highest volume of biogas was 6540Lit and with a methane content of 72.05% this produce produced by the digester containing 75% Water Hyacinth waste and 25% tannery solid waste. The lowest biogas concentration (2540Lit) of methane concentration 68.06% was produced by digester containing tannery solid waste alone.

Key Word: Biogas, Tannery flesh waste, Water Hyacinth, Cow Dung, Anaerobic digestion

Table of Contents

List of Figures

List of Tables

Acknowledgment

God comes first for all the blessings and also for the fact that the thesis is finally over. For any work to be prosperous the contributions of people involved are ultimate. I take this opportunity to convey my heartfelt gratitude and acknowledge for those who help, support and giving guidance for this work. Foremost, I would like to acknowledge the support, immaculate guidance and friendship of my advisor, Dr. Ing. Anuradha Jabasingh (PhD); for her guidance. I would like to express my sincere gratitude to my advisor for her willingness and keen response when I asked her to update(reinstatment) myself as post graduate student. I would also like to extend my thanks to all staffs of Center for the ELCO leather PLC. and the laboratory staffs of Addis Ababa University for their help during this thesis work. Warm thanks also go to ELICO Tannery Share Company and their staffs for allowing me to take samples and other crucial documents that help me to get full information about the tannery and who made this assignment both successful and extraordinarily pleasant. In addition, my thanks extend to all who edited this document, and made it readable especially, my brother Ato Endalkachew Mamo. Thank you all for your immeasurable efforts and time. My special thanks go to all my colleagues in postgraduate class and all others who are with me in all aspects during my graduate study. Last but surely not the least; I owe my loving thanks to my mom for her multifaceted support, ongoing conviction in me and motivating me to keep on working towards a sustainable future.

Acronyms

AD	Anaerobic digester
AMCAN	Addressing climate change challenges in Africa
BBD	Box Benkhen Design
C/N	Carbon (total organic) to Nitrogen ratio
EEPA	Ethiopia environmental protection agency
ELIA	Ethiopian leather industries association
HRT	Hydraulic retention time
IPCC	International panel on climate change
LIDI	Leather industry development institute
OLR	Organic loading rate
RT	Retention time
RSM	Surface Response methodology
SRT	Solid retention time
TS	Total solid
TSW	Tannery solid waste
UNFCCC	United nations framework convention on climate change
UNIDO	United nations industrial development organization
USEPA	United states environmental protection agency
VOCs	Volatile organic compounds
VS	Volatile solid
CDM	Clean development mechanism
WH	Water hyacinth

Chapter One

Introduction

1.1 Background

The production of energy from non-renewable sources affects both socio-economic and environmental developments which in turn affects the livelihoods, access to safe water, agricultural productivity, health, education and gender related issues (Hossain, 2010). The production of energy from renewable sources is one of the main strategic tools for the sustainable development of current society all over the world. Clean energy supply is crucial to ensure sustainable economic development in any country (Omer, 2010). Thus, looking for alternative sources of energy is vital (Abdeen,2010). Using renewable sources for energy production has benefits that lead to environmentally friendly sustainable forms of energy (Omer, 2010,). Biomass waste from industries can be used as a source of renewable energy as well as an alternative to fossil fuels is attracting great attention. They are an unavoidable byproduct of human activities (Qurashi & Hussain, 2005).

The environment is under increasing pressure from solid and liquid wastes emanatingfrom industries, such as tanneries. Disposal of untreated wastes into land and waterbodies from tanneries results in water and air pollution as well as emission of greenhousegases like methane and carbon dioxide, This. problemcan be mitigated through the adoption of eco-friendly waste-to-energy recycling technologies for treatment and processing of wastes before their disposal (Vasudevan and Ravindran,2007).

Biogas plants are multipurpose biological processing plants that can be implemented for various reasons. It also provides some exciting possibilities and solutions to such global concerns as alternative energy production, handling human, animal, municipal and Industrial wastes safely, controlling environmental pollution, and expanding food supplies (Marchaim, 1992). Electricity produced from biomass fuels is considered to be renewable, because carbon dioxide produced by the generation process is sequestered again when the biomass crop (or other biomass source) grows. Although results differ between life cycle analyses of biomass technologies, it is apparent that the technology hasthe potential for very low life cycle greenhouse gas emissions rates or may even achieve more than complete closure of the carbon cycle (i.e. carbon-negative) when chemical absorption of CO_2 is employed (Carpentieri *et. al.*, 2005).

In Ethiopia, the generation of industrial waste, including hazardous waste, is increasing rapidly as a result of urbanization, the implementation of a new economic policy and industrialization. While the Ethiopian economy grew by 1.9% in the period 1980 to 1990in tangible terms, the toxic load generated per unit of industrial output augmented by 1.8% which is higher as compared to the Sub- Saharan Africa average of 1.3% (LIDI, 2010).In addition, industrial wastewater has become one of the most serious problems because of the increase in the discharge of untreated effluent to the environment.
Many industries fail to afford investments in pollution remediation equipment and technologies, because their profit margin is very low (EEPA 2010). Thus, it has become imperious to prevent or at least diminish the generation of wastes in the first place, a concept known as pollution prevention‟ or „waste minimization‟ by treating the wastes from the industries. The government plans to increase the number of tanneries during the coming five years due to the high demand in the international market for leather and leather productsand Ethiopia earns substantial amount in foreign exchange from leather and leather products exported. In the last decade the tanning industry increased remarkably andthe export earnings from the sector has been in the order of a hundred million dollars ranking second to that of coffee. Though tannery is a major export industry,the pollution and greenhouse gases emission associated with it is a major concern.Moreover,tanning process is water intensive and tannery waste water containslarge amount of hazardous chemicals (European Commission, 2003).
Therefore, ultimate tannery waste management approach in general, should safeguard public health and the environment, diminish the burdens on current and upcoming generations, conserve resources, and minimize cost. Carefully planned and implemented anaerobic digestion facilities can accomplish all of these goals (leung and wang, 2016).

Anaerobic digestion (here after AD) is a biological process typically employed in many wastewater treatment facilities for sludge degradation and stabilization, by a consortium of microorganisms working synergistically (Joshua. *et al*, 2009). In practice, microbial anaerobic conversion to methane is a process for effective waste treatment, biological fertilizer and sustainable energy production. It has the potential for reducing the use oftraditional biomass, the demand for fossil fuels like coal, oil, and natural gas which continued exploitation will significantly impact our environment and affect the globalclimate (Wilkie, 2008).

Furthermore, AD is a promising, mature and recognized technologic solution that have the potential to convert tannery wastes into energy efficiently (biogas), elimination of uncontrolled methane emissions and odour, contributing to lessen the environmental problem, safe waste management, giving time to set-up more sustainable treatment and disposal routes (Vasudevan and Ravindran, 2007).

Therefore, a well-designed AD fosters sustainable development since it recovers energy thus reducing fossil fuel use and reducing greenhouse gas sources. Another factor that has triggered opting for energy recovery from waste is international agreements like, Kyoto Protocol, a supplementary treaty to the United Nations Framework Convention on Climate Change (UNFCCC) the emissions reduced from the clean technology could generate carbon credit under the Clean Development Mechanism (CDM) which is additional incentive to be clean with respect to greenhouse gas emissions (Marchain, 1992). According to Reijnders and Huijbregts (2007), the potential for waste-derived bio-energy to contribute to the bargain of global warming is great. Moreover, AD technology can play a key role in realizing three major international environmental policy objectives of renewable Energy, water Pollution, Kyoto Protocol / Global Warming.

Thus, the best strategy is to manage and utilize tannery waste as “biomass” resources rather than disposing of as “waste” so that energy and economic benefits, as well as environmental benefits, can be realized. AD of tannery waste significantly reduces the gaseous emissions (CH4 and CO2) from waste disposal (Buren, 1979). Hence, anaerobic digestion of tannery waste would be a better way of waste utilization for energy generation and waste management. In view of this, the present research is aimed to study the efficiency of AD of tannery waste for renewable energy production and waste management. Investigations on the viability to mitigate greenhouse gas emission with this technology will also be carried out.

1.2 Statements of Problem

Biogas is one of waste to energy conversion technology. In time different research have been done on biogas production. Researches show that it is better to use co-digester than single waste digester and the optimum production of biogas was obtained at temperature of 35°C and pH 7 (Gidey, 2017), generating biogas from cow dung and cactus fruit peel which deal on efficiency of biogas produced. The research result show that when the ratio of cow dung to fruit peel is 75 gram to 25 gram optimum yield was attend also is efficient (Meseret, 2016). The other research done on this area was investigating problem and suggesting solution for biogas generation from agricultural waste.

- This research gives direction to the farmers since they don't have idea on how biogas generated but their cattle generate a lot of waste which pollute environment if managed properly. If they could generate biogas from agricultural waste the can get electrical energy, minimize green gas effect, can get compost or organic fertilizer (Saidmamatov et al., 2021).
- The present research on biogas production from anaerobic digestion of water hyacinth and tannery solid waste using inoculum from cow dung was take to investigate efficiency of bio gas production by the integration of water hyacinth and tannery flesh waste using cow dung as source of microbial inoculum and one of biogas production ingredient.
- This research also characterizes the raw ingredients, investigates the effect of retention time, mass variation of water hyacinth and tannery flesh, and optimize biogas the production.
- Over all to remove Water Hyacinth from the lakes easily and tannery flesh waste is headache and bulky amount of waste in Ethiopia. It is the main problem in our country so that investigating and doing more research on biogas production is the best way for removing the problems of water hyacinth.

.

1.3 Objectives

1.3.1 General Objective

The General objective of this study is to investigate the biogas production potential from a mixture of water hyacinth and tannery flesh waste by using in cow dung as inoculum with anaerobic digestion at laboratory scale.

1.3.2 Specific Objectives

- To investigate the effect of retention time, water hyacinth concentration and tannery flesh waste concentration on the methane yield.
- To determine the amount of waste reduced after the biogas production by anaerobic digestion in term of COD, BOD, TS, VS, TN
- To determine the optimum operation parameters using response surface statically methodology.

1.4 Significance of the study

This research has many significance for the country as well as for researchers. It fills the gap of feed stock for biogas production and give optimum operation parameters for the generation of biogas from water hyacinth and tannery flesh waste by inoculating in cow dung. Waste generated from cow or cow dung are the main source for green gas which pollute environmental air. But this research helps to reduce the pollution and let the societies to get energy from the waste. In addition to this the research uses tannery flesh as one of feed stock this when used for production of biogas reduce the waste generated from the tannery industry and it became source of energy or income. Water hyacinth commonly in local name called Emboch wa used used as feedstock along with tannery waste.

CHAPTER TWO

Literature Review

2.1 Tanning Industries and Process

Raw skin and hides are wastes from sheep, cattle, and others in slaughterhouse which needs to be collected and converted to a usable product. The process by which this collected waste from slaughterhouse converted to a usable and stable product that is resistant to microbial attack, wet and dry heat is known as tanning. It was therefore a way to reutilize a waste, if not a waste to become decay and unusable (Anthony, 1997; Favazzi A., 2002). It consists of a sequence of successive operation converting raw hide and skin into leather (Anthony, 1997). The process begins with selection, trimming, i.e., removing the extra part of the skin and soaking (Mekonnen Bekele and Gezahegn Ayele, 2008). An intermediate product from tanning industry that has various applications once produced is known as leather. Staring from an ancient time human being was using leather. Most production process in tannery is operated in batch with sequential orders: namely, beam house (pre-tanning), tanning (tan-yard), wet finishing (post-tanning) and finishing operation.

In the beam house operations, once hides and skins are delivered, they can be arranged, trimmed, cured and stored pending (soaking, removal of extraneous tissues, deliming, bating, pickling and degreasing) operations are typically carried out in the beam house (European commission, 2003; Cotance, 2002). Tanning operations stage is the most fundamental one which gives leather its stability and essential character, which is either done by chrome or vegetable tanning method. The tanning agent and the collagen fiber make a cross-linking action so that the hide is no longer vulnerable to putrefaction or rotting (European commission, 2011). Post-Tanning Operations is the third stage which involves washing and neutralization, retaining, dyeing, fat-liquoring and drying in which specialist operation can be carried out to add certain properties to leather. Finishing operations is the concluding stage which with total objective to enhance the appearance of the leather and to offer the enactment characteristics with respect to color, gloss, handle, etc (Cotance, 2002).

2.1.1 Waste Management in Tanneries

The environmental quality has been an issue of concern in the conditions of increasing urbanization, industrialization and vehicular pollution as well as pollution of water courses due to release of effluents without checking to the environmental norms and standards (Kanagaraj *et al*, 2006). The concept of waste management involves the collection, removal, processing, and disposal of materials considered waste. Waste materials can be solid, gaseous, liquid, or even hazardous and are generally generated through human activity).The tanning industry is characterized by disposing of solid, liquid, gaseous and sludge wastesto the environment which have a serious effect in contaminating of fresh water bodies,soil, and streams with the highest toxic concentration per unit of output (Singh *et al.*,2011; Durai and Rajasimman, 2011).

Waste management in tanning industries has received a great emphasis as more severe effluent standards have been adopted. Like the tanning industry in the world, the problemof treatment and discarding of their wastes is probably as old as the industry itself. That is poor management practices in the tanning segment have led to a substantial degradation over time in environmental quality. The challenges of meeting rising needs are discouraging, but it is important to hassle that the condition is not hopeless. In recent days, sustainable development is in the first place on the tanning industry agenda. The amount of generated wastewater and solid waste continuously increases and due to the large environmental impacts of its improper treatment, its management has become social and an environmental concern. EEPA (2005) showed the annual volume of liquid waste discharge from the 15 tanneries in Ethiopia based on their annual production capacities is estimated to vary between 2,000,000 and 2,500,000 cubic meters. Thus, are causing serious environmental and public health problems in particular and in urban centers and further extend to rural areas as well. Besides, the loss of economic benefits that could have been derived from this sector, cannot survive a growing challenge of environmentally sound competitive business unless appropriate environmentalmanagement system is introduced.

The absence of appropriate environmental laws and standards as well as low level of environmental awareness, lack of effective implementation of legislative control, location of the tanneries in urban centers (non-industrial zone areas) along multipurpose rivers and streams, the absence of treatment facilities, poor processing practices, use of unrefined conventional leather processing methods and poor environmental management systems are aggravating the situation (Khan *et al.*, 1999). Hence, it is essential to change this situation by familiarizing a system that helps improve the environmental performance and as a result the productivity of tanneries in all aspects. Biological conversion of biomass to methane has received increasing attention in recent years. There are several technologies like incineration, AD and refuse derived fuel etc., for producing energy from solid wastes. Among them, AD has come to be a promising technology mainly for recovery of energy from organic fraction of solid wastes and become a major focus of interest in waste management throughout the world (Tamilchelvan and Dhinakaran, 2012).

Anaerobic digestion (or bio-methanation) systems are mature and proven processes that have the potential to convert tannery wastes into energy efficiently, waste management and achieve the goals of pollution prevention/reduction, elimination of uncontrolled methane emissions and odor, through recovery of bio-energy potential as biogas, pre production of stabilized residue for use as low grade fertilizer. In addition, it is afavorable, ideal and technological solution which degrades a substantial part of theorganic matter contained in the sludge and tannery solid wastes, generating valuablebiogas, contributing to alleviate the environmental problem, giving time to set-up more sustainable treatment and disposal routes (Kaul *et al.*, 2001).

2.1.2 Tannery Waste Generation and its Environmental Impacts

Globally tanneries are categorized among the oldest and fast growing industries which have intensive pollution impact on the environment. It is the most challenging globally in terms of environmental regulation (Durai and Rajasimman, 2011). Their impact on environment is originated not only from wastewater, solid and gaseous waste streams and but also from the raw materials inputs like, energy, water and chemicals. Fleshing,shaving, sludge of wastewater, beam house and splitting are among the main potential source of solid waste while beam-house, the tan-yard, and the post-tanning operations in wet processing are the main potential sources of wastewater and dry finishing is the main source of gaseous emissions pollution in tanneries (Ane, 2000; European commission, 2003).

From one tone of raw hide/skin it is expected that an average of 200-250 kg of leather produced, which results in the generation of more than 750-800 kg of solid waste and about 30-50 m^3 of wastewater and 40 kg of air emission (Buljan *et al.*, 2000; Kanagaraj *etal.*, 2006). Therefore, in the processing of the hides/skins only 20-25% of the weight of the raw hide/skin is converted to leather, based on the other things, like the animal species and product specification (Buljan and Bosnic, 2006). The nature and load of the solid waste and wastewater depends on the kind of production process (different producers) and technology used (European commission, 2003). Among the three impacts of tannery waste on environment, air pollution impact takes the least share while wastewater pollution impact takes the highest share, hence is the most serious threats to the environment (Javed . *et al.*, 2000).

Therefore, tanning industry waste poses severe environmental impact on water (with its high COD, discoloration and toxic chemical constituents (Song *et al.*, 2000), terrestrial and atmospheric systems. Tannery waste typically contains a complex mixture of both organic and inorganic pollutants (Reemste and Jekel , 1997; Mwinyihija, 2007).

2.1.3 Tanning Industry in Ethiopia

Ethiopia‟s Industrial Development Strategy prepared in August 2003 prioritizes the leather product industry together with garment/textile, meat processing, construction, small and medium sized enterprise industries. Tanning industry contributes significantly towards exports, employment opportunity and occupies an important role in developing countries economy on the other hand (Soyalsan and Karaguzel, 2007). According to the Ethiopian Leather Industries Association‟s website (ELIA, 2012), Ethiopia is one of the top ten countries in the world that are endowed with abundant livestock resource (50 million cattle, 25 million sheep and 23 million goats). As a result of this, leather has been at the core of Ethiopia's economy since many decades. About 80% of all hides and skins entering the formal market are from rural areas where they are collected by private traders. The remaining 20% are derived from slaughtering facilities in major towns and cities. There are about 1500 registered private traders dealing in raw hides and skins (ELIA, 2012).

The Ethiopia‟s leather industry has seen important advancements for example, the number of tanning companies, that were a handful ten years ago, have now rose to twenty six with more under formation (ELIA, 2012). All of them are of considerable size with the smallest having a soaking capacity of 3000 skins per day (with one shift). These days in Ethiopia leather industry is an important strategic sector for the economic and industrial development of the country and significantly contributes to the nation‟s export earning with about 95 million USD. Ethiopian leather industry is endowed with one of the richest sources of raw material interms of both quality and quantity in African continent and has been reliably figuring in the grade of 30 upper most countries contributing to the raw material base for the global leather industry. Nonetheless, Ethiopia has a large livestock population; the tanning sub-sector is considerably lags behind many countries that are less gifted. This is why some tanning industries in Ethiopia are operating at much below their full capacity due to various factors. In addition to this, before a year most tanning industry in Ethiopia limited to production of wet blue and even that not of high quality. According a survey carried out by the Ethiopian Economic Policy Research Institute, the tanning industry in Ethiopia functions on average, at two-thirds of its full potential. Ethiopian government has given attention to the leather industry, being the largest manufacturing industry which has the potential to contribute significantly to the export earnings of the country on one hand and employment opportunities on the other. Hence, it is trying to catalyze the growth of the industry through policy interventions and intensive technology up-gradation, programs through bench marking projects for tanning and foot wear industries which is currently leaded by Ministry of Trade and Industry of Ethiopia

This shows the tanning industry in Ethiopia is on the way to change itself from a traditional industry to a modern industry to infiltrate the international high value-added leather market, under the strong initiative of the government (EuropeanCommission, 2003).

Ethiopian tanning industry like tanneries in the world is labor, material, energy and water intensive. Hence, it generates large quantity of wastewater containing high amount of BOD, COD, TDS and sulfide (EEPA, 2005). Most of the tanneries in Ethiopia discharge their wastewater to the environment. The solid wastes generated are used to be disposed to the landfill. This causes a serious environmental degradation unless it is managed. Prior to discharging their wastewater to environment some tanneries have primary or secondary wastewater treatment plant while none of them have solid waste management system. The wastewater released from tanneries to the environment easily contaminates the surface as well as the underground water thus bargaining the quality of potable water. The solid waste from all tanneries either burned without proper incinerator or disposed to open landfill as indicated in figure 1 below. Burning and disposing solid waste on open damp fill, in addition to releasing greenhouse gases from the decomposition of organic matters, it produces undesirable odors posing health hazardous to community (DivakaranS., 1984).

Ethiopia environmental protection agency set provisional limit for tannery effluent discharge which do not give permission for implementing new tanneries without an effective effluent treatment plant (Favazzi , 2000).

2.2 History of Anaerobic Digestion for wastewater management and treatment

Anaerobic digestion for management of wastewater has been started from the time Mouras, a Frenchman, applied anaerobic digestion to treat wastewater in 1881 (McCarty *et al.,* 1982). Next Cameron, an Englishman, constructed a tank in 1895 which was similar to Mouras‟s "automatic scavenger" nevertheless had better treatment efficiency, and named it "septic tank". Moreover, the value of the methane gas which was generated during sludge decomposition in the septic tanks was recognized by Cameron and certain gas was used for heating and lighting purposes at the disposal works (Chawla, 1986). Treating high COD waste rather than as a means of generating energy (biogas). Anaerobic digestion dates back as far as the 10th century, when the Assyrians used it to heat bath water. It was historically insignificant before reappearing in 17th century Europe, when it was determined that decaying organic matter produced flammable gases, again used to heat water. The first full scale application was in the 1890s when the city of Exeter, England used it to treat wastewater. From there, it continued to be widely used as a way to stabilize sewage sludge, as it is today (Mahony *et al.*, 2002). The first systems were large, unheated and unmixed tanks with significant operational problems due to solid settling and scum formation. These frequent system disturbances limited the adoption of the technology until the twentieth century (Ostrem, 2004).

Recently, improvement continues on farms as well as wastewater treatment plants, where AD processes and subsequent gas recovery are an industry standard. AD has conventionally been used to treat liquid wastes with or without suspended solids such as manure, sewage, industrial wastewater and sludge from biological or physic-chemical treatments. During the anaerobic digestion process, the microorganisms present in wastewater sludge decompose organic matter in the absence of oxygen to produce a gaseous mixture of carbon dioxide (CO_2) and methane (CH_4), referred to as “biogas”. Anaerobic wastewater treatment is generally a more environmentally friendly treatment technology than aerobic treatment due to its low solids generation rate, low electrical energy requirements and the production of a usable biogas. In comparison, solid wastes such as agricultural and municipal solid waste had attracted comparatively little attention from AD specialists till recently (Mata-Alvarez, 2003).

According to Mata-Alvarez (2003), among biological treatments, AD is frequently the most cost-effective, owing to the high energy recovery linked to the process and its limited environmental impact. Moreover, Vogt *et al.* (2002) reported that AD of biomass waste was now an established and commercially proven approach for treatment and recycling. AD of municipal solid waste was the preferred approach and reliable technology for the provision of energy and reduction of greenhouse gas emissions when compared to combustion/incineration, aerobic composting, pyrolysis and landfilling/landfill gas recovery.

In recent decades, anaerobic digestion of bio-waste has been studied intensively with the objective to develop a technology that offers waste stabilization with resources recovery (Nguyen *et al,* 2007). Major motivating forces behind the growth of AD technologies for bio-waste in Europe have been limited landfill capacities with increasing tipping fees, subsequent legislation on progressive removal of landfilling of organic waste (Landfill Directive, 1999) and recently declared renewable energy laws trying to encourage and assist sustainable energy production (Nichols, 2004). AD is currently considered to be a proven and trustworthy technology used to treat more than 10% of organic waste in several European countries (Baere D., 2000). Also on a worldwide scale, anaerobic digestion of bio-waste has by now become an established biological treatment technology(Gebren & Oelofse, 2009). It is mainly the beneficial recovery of energy as well as the recovery of nutrients which make anaerobic digestion of bio-waste a sustainable and prized treatment perception (Hartmann & Ahring, 2006).

Moreover, AD was considered to be feasible for high strength wastewater and only for temperature conditions above 20–25 (Kalogo & Verstraete, 2001) so that the first anaerobic reactor configurations were designed for industrial wastewater treatment. In addition, the net production of excess sludge is also lower and the methane gas produced can be used as energy source. The AD of high strength wastewater in temperate climate countries is the appropriate choice because the great volume of methane gas produced is used to heat the reactor to a desired operational temperature (30–35) (Lettinga, 2001).

2.2 Biogas as Energy Source

Biogas is a combustible gas, which is from biodegradation of organic material under anaerobic situations mainly containing methane (CH_4) and carbon dioxide (CO_2) that can be used for heating and electrical power generation. In this process, a source of renewable energy, biogas is generated. Biogas production from agricultural, municipal industrial wastes through anaerobic digestion can contribute to sustainable energy production, especially, when nutrients conserved in the process are returned to agricultural production (Wilkie, 2008). APCAEM (2007) stated that the composition of biogas might vary according to the experimental situation, digester type and the substance that being used as feedstock. If the feedstock material contains of mainly carbohydrates such as glucose and sugar low amount of methane is produced while if the feedstock material has high fat content production of methane is high.

2.2.1 Amount of Methane in Biogas

Biogas is a mixture of gases, mainly methane, and carbon dioxide, resulting from the anaerobic fermentation of organic matter and can be used as a fuel for heating or electrical power generation. It usually contains 50% and above methane and other gases in relatively low proportions namely, CO_2, H_2, N_2 and O_2 (Milono *et al.,* 1981; Kalia *et al.,* 2000). The mixture of the gases is combustible if the methane content is more than 50% (Agunwamba, 2001). Methane potential fraction differs and ranges between 40%-80% on the basis of the digester type, substrate quality and digesting bacteria (Stewart *et al.*, 1984).

Yadav and Hesse (1981) reported that biogas is the mixture of gas mainly composed of 50-70 percent methane, 30 to 40 percent carbon dioxide (CO_2) and low amount of other gases like water vapor, hydrogen sulfide, hydrogen, and nitrogen. Marchaim (1992) reported that typical values for methane content are in the range 50- 60% CH_4 for animal manure and up to 75% CH_4 for feedstock containing fats. The proportion of CH_4 to CO_2 in the gas depends on the substrate and is slightly affected by temperature, pH and pressure. Water hyacinth and cow dung were mixed in the ratio of 3:2 and the gas produced was found to contain 25-32 percent carbon dioxide (Anonymous, 1981).

2.3 Anaerobic Digestion

The AD process, also referred to as bio-methanization can be presented as a series of biochemical and microbiological phases in which microorganisms degrade biodegradablesubstrate (feedstock) in an oxygen free environment resulting in the production of biogas which is rich in methane (CH_4) (Ciborowski, 2004). The hydrolysis bacteria breakdown insoluble organic compounds like proteins, carbohydrates to make the feedstock easily available for other group of bacteria to start up the process. Amino acids and organic acids are converted into carbondioxide, hydrogen, organic acids and ammonia. Then, the organic acids are converted to acetic acid, along with additional hydrogen, ammonia and carbondioxide by acidogenic bacteria. Finally, the end result of the above bacterial actions converted to methane and carbondioxide by methanogenic bacteria (Pena-Varo, 2002).

Anaerobic decomposition occurs extensively in: water-logged soils and rice fields, swamps, deep bodies of water, and in the digestive systems of ruminant animals. AD processes can be managed in a digester or enclosed lagoon for waste treatment. Organic waste such as human manure and livestock, and several types of bacteria are put in an airtight container so the process could occur. Nowadays, AD of those organic wastes is usually used as a means of production of energy and pollution control (Fabien M., 2003). Moreover, engineered anaerobic digesters are to treat high-strength industrial and food processing wastewaters prior to discharge (Kalogo & Verstraete, 2001), with the foremost benefits of biogas production, nutrient recycling, waste treatment, waste management, GHG reduction and odor control. Depending on the system design and the type of feedstock waste, 55-75 percent of biogas is pure methane (Williams, 1998;Ostrem, 2004).

2.3.1 Basic Principles in Anaerobic Digestion

AD is a multifaceted process that comprises collaboration between many different microorganisms, so-called conglomerates; which survives optimally at a given set of chemical and physical conditions (Pena-Varo, 2002; Mata-Alvarez, 2003). The degradation in AD processes can be divided into four major phases: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Veeken *et al.,* 2000). Each of the four steps depends on certain microbial conglomerates to perform the conversion processes. Some conglomerates are extremely tolerant and can use multiple substrates (feedstock), while others are very sensitive towards environmental fluctuations and in addition are only proficient of using a single substrate. Therefore, in order for the four degradation steps to be in equilibrium, the overall chemical and physical environment in the biogas reactor has to fulfill the needs of all consortia at all time (Teodorita, 2007).

Hydrolysis

Hydrolysis is the first step in the anaerobic digestion (degradation) process. Hydrolytic and fermentative microorganisms excrete hydrolytic enzymes that convert biopolymers into soluble compounds. Lipids, polysaccharides, nucleic acids, and proteins are converted to mono- and oligomers such as glycerol, glucose, Purines & Pyrimidine, and amino acids. It is an important step enabling fermentation and subsequently biogas formation (Teodorita, 2007; Larry *et al.*, 2004). Whereas some of the products of hydrolysis, including hydrogen and acetate, may be used by methanogens later in the anaerobic digestion process, the majority of the molecules, which are still relatively large, must be further broken down in the process of acidogenesis so that they may be used to create methane.

Acidogenesis

Acidogenesis is the next stage of AD process in which acidogenic bacteria further break down the end products of hydrolysis. These fermentative bacteria produce an acidic environment in the digestive chamber while creating ammonia, H_2, CO_2, H_2S, shorter volatile fatty acids, carbonic acids, alcohols, as well as trace amounts of other byproducts (Pena-Varo, 2002; Veeken *et al.*, 2000). Acidogenesis is usually the fastest step in the anaerobic transformation of complex organic matter in liquid phase digestion (Bjornsson, 2000). Even if, acidogenic bacteria further breaks down the organic matter, it is still too large and unusable for the ultimate goal of methane production, so the biomass must next undergo the process of acetogenesis (Ostrem, 2004).

Acetogenesis

Acetogenesis is the acetate formation stage, a derivative of acetic acid, from carbon and energy sources by acetogens. Acetogens catabolize many of the end products created in acidogenesis into acetic acid, CO_2 and H_2 (Pena-Varo, 2002; Veeken *et al.*, 2000). Biological oxygen demand (BOD) and chemical oxygen demand (COD) are reduced through these pathways (Ostrem, 2004).

Methanogenesis

Methanogenesis constitutes the final stage of anaerobic digestion in which methanogens create methane from the final products of acetogenesis as well as from some of the intermediate products from hydrolysis and acidogenesis. The operating conditions have severe influence on the methanogenesis (Teodorita, 2007) Even if, CO_2 can be converted into methane and water through the reaction, the main mechanism to create methane in methanogenesis is the path involving acetic acid. This path creates methane and CO_2, the two main products of anaerobic digestion (Veeken *et al.*, 2000).

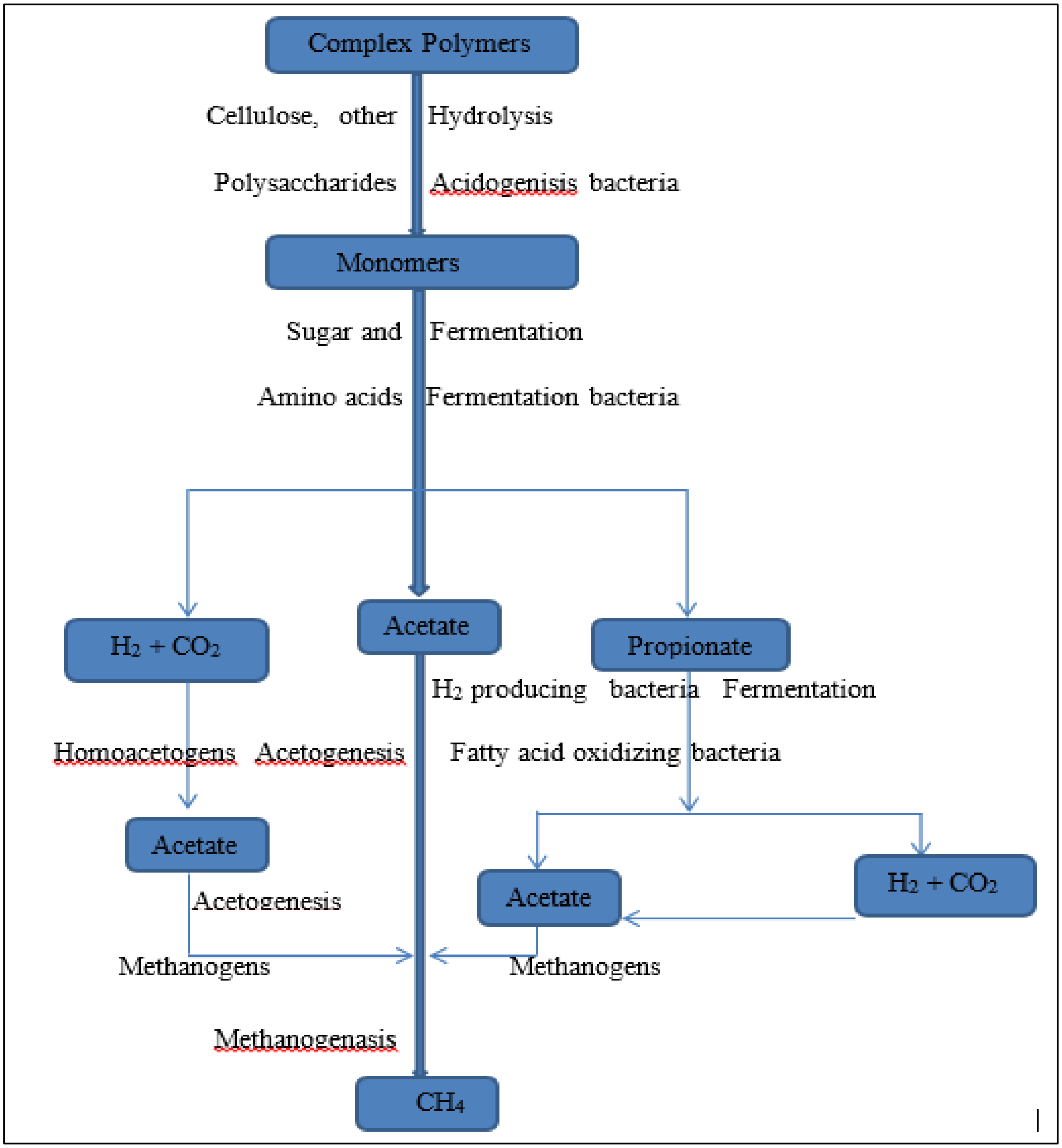

Figure 1: Anaerobic Digestion Process (Madigan et al., 2003)

2.4 Factors Affecting Anaerobic Digestion

The complete process of anaerobic digestion needs a complex interaction of several varieties of bacteria that must be in equilibrium in order for the digester to remain stable. Variation in environmental conditions can disturb the equilibrium and leads to buildup of intermediaries that can inhibit the biogas production process or shut it down altogether. Itis important to take care off and use design control technologies to incessantly monitor and adjust the environment to avoid the inhibition due to environmental variation.

There are so many factors within the digester that have impact on the physical environment, the rate of digestion and biogas production. Good performance of biogas plant can be controlled by monitoring the variation in parameters like C/N ratio, organic loading rate, temperature, Hydraulic retention time (HRT), pH, percentage of solids, toxic substances and etc. Any radical change in these parameters can detrimentally affect the biogas production. Therefore, these parameters should be varied within an appropriate range for efficient function of the biogas plant (Vlyssides and Karlis, 2003).

2.4.1 Temperature

Temperature is important operational parameter which has strong influence on AD process. The rate of anaerobic degradation processes specifically the rate of hydrolysis and methanogenesis depended on temperature. As stated by Mital (1996) there are three different temperature ranges at which anaerobic bacterial operate. Psychrophilic bacteria operate best between 10 and 20 , mesophilic 30 and 40 and thermophilic 45 and 60 . AD is very efficient in thermophilic range, but rural type digester uses mesophilic bacteria as temperatures higher than 35 are very hard to obtain. Optimal temperature for mesophilic bacteria is 35 and 55 for thermophilic bacteria (Marchaim, 1992). Meta–Alvarez (2002) witnessed that at low temperature (14 -23) reasonable gas yield will be expected from AD.

Bacterial population in anaerobic digester are hardly resistant to short term upset of temperature of two hours, and back to rapidly to normal gas production rates when the temperature is restored. Unbalanced population of bacteria will result as the temperature drops is prolonged and lead to low pH condition (Marchaim, 1992). Thermophilic digestion allows higher loading rates and achieves a higher rate of pathogen destruction as well as a higher degradation of the substrate. It is, however, more sensitive to toxins and smaller changes in the environment and is less attractive from an energetic point of view since more heat is needed for the process (United Tech, 2003). Furthermore, thermophilic condition needs a month or more to establish a population (Golueke, 2002).

Bacteria operating in the mesophilic range are more robust and can tolerate greater changes in the environmental parameters, including temperature. Temperature fluctuations can be extreme in smaller digesters, poorly insulated digesters or digesters in cold climates, suggesting that these would benefit by being run in the mesophilic range to diminish system crashing. The stability of the mesophilic process makes it more popular in current AD facilities, but at the expense of longer retention times. Therefore, temperature needs to be carefully monitored in all modern digestion facilities through temperature probes at various locations in the digester chamber. Moreover, the digestion process should be designed to operate at constant temperature. In general, temperature has a positive effect on the rate of AD, which will produce higher methane volume (Michael, 1979).

2.4.2 pH

Level of pH is a primary indication factor of digester health as the enzyme in the anaerobic reactor is sensitive to specific and narrow pH range, which changes in response to biological conversation during the different processes of AD. Acceptable pH range for the bacteria take part in anaerobic digestion is from 5.5 to 8.5, even though, the optimal pH value for acidogenesis and methanogenesis stages are different (Golueke, 2002; RISE-AT, 1998). In the systems in which both coexist, the optimal pH range is 6.8–7.8 (Boopathy, and Daniels, 1991). The amount of carbon dioxide and volatile fatty acids (VFA) produced during the anaerobic process affects the pH of the feedstock in the digester. For an anaerobic fermentation to go ahead normally the concentration of volatile fatty acids acetic acid in particular should be below 2000 mg/l. Methane production efficiency was more than 75%at pH greater than 5.0 (Mattiasson and Jain, 1998).

Accumulations of acid have a great problem for digester failure. This would happen if theamount of volatile solids loaded into the digester as fresh waste increased sharply. The acidogenic bacteria would then thrive, producing high volumes of organic acids and lowering the pH to below 5.0, a level lethal to methanogens. This creates a positive feedback loop as a declining methanogens population will in turn lead to further acid accumulation as the methogens are responsible for consuming acids. An acidic pH indicates that the process has already begun, and immediate action is required, such as recycling more water. On the other hand, prolific methanogenesis may result in a higher concentration of ammonia, increasing the pH above 8.0, where it will impede acidogenesis (Lusk, 1999).

According to Marchaim (1992), two major operational approaches are used to correct the unbalanced low pH condition in a reactor. The first method is addition of chemicals to raise the pH which will provide additional buffer capacity. The second method is to stop the feed and allow the methanogenic population time to reduce the fatty acid concentration and hence raise the pH to an acceptable level. Healthy digester requires carefully controlled raw materials in digester. The former have an advantage of stabilizing the pH immediately, and the unbalanced population allowed correcting themselves more quickly.

2.4.3 Carbon to Nitrogen Ratio (C/N)

Drawnel (2008) and Pyle *et al.* (1978) reported optimal C/N ratios in AD should be from10: 1 to 25: 1 and 10-30 respectively. A high C/N ratio is an indication of a rapidconsumption of nitrogen by methanogens and results in a lower gas production. On other hand, a lower C/N ratio causes ammonia accumulation and pH values exceeding 8.5, which is toxic to methanogenic bacteria. A low C/N ratio, or too much nitrogen, can cause ammonia to accumulate which would lead to pH values above 8.5 (Vlyssides and Karlis, 2003). To obtain the optimum mixing ratio waste material that is low in carbon content can be combined with materials having high in nitrogen content to attain desired C/N (Barnett A., 1978; Fry and Merill, 1973; Gotass, 1956; Singh, 1974). For optimum growth the bacteria in the AD process requires micronutrients and trace elements such as sulphur, potassium, calcium, magnesium, iron, nickel, cobalt, zinc, manganese and copper. Although these elements are needed in very low concentrations, the deficiency of these nutrients has an argumentative effect upon the microbial growth and performance (Singh, 1974).

The microbial population participated in AD needs nutrients to multiply and grow. The elements carbon and nitrogen in the feedstock are the main foods of anaerobic bacteria. C/N ratio represents the relationship between the amount of carbon and nitrogen present in organic materials. Carbon is responsible for energy production while nitrogen for building cell structure. Therefore, it is necessary to maintain proper composition of the feedstock for efficient digester operation and proper proliferation of bacterial so that the C/N ratio in feed remains within desired range. The decomposability of the carbon and nitrogen sources also plays a great role to get the suitable carbon/nitrogen (C/N) ratio (Joshua R. *et al.*, 2008).

2.4.4 Retention Times

The time required for a complete degradation of organic matter in the anaerobic digester is called Retention Time (RT), the longer a substrate is kept under proper reactionconditions, the more complete its degradation will be. The rate of the reaction, however, will decrease with increasing residence time, indicating that there is an optimal time that will achieve the benefits of digestion in a cost effective way. Environmental conditions, intended use of the digestate, composition of feedstock, COD and BOD of exiting effluent (of the feedstock) are some of the parameters that determine the RT (Xinyuan, 2010; Mahony, T. *et al,* 2002; Zennaki *et al.,* 1996; Singh *et al.,* 1995; Garba, 1996).

2.4.5 Hydraulic Retention Time (HRT)

The average time in which the liquid feedstock is detained in the digestion process till the gas production ceased is called Hydraulic Retention Time (HRT). Though, standard hydraulic retention time for a co-digestion of different waste in AD process without sludge recycle is 15-30 days, HRT varies from 30–50 days in hot climate countries while in countries with colder climate it can extend to 100 days. Washout of active bacterial population and larger volume of the digester which will pose high capital cost is the disadvantage of Shorter and longer HRT respectively. Without stressing the fermentation process at mesophilic and thermophilic temperature ranges it is conceivable to carry out methanogenic fermentation at low HRT‟s (Zennaki *et al.*, 1996; Singh *et al.*, 1995; Garba, 1996). Some other factors are;

Biological Solid Retention Time (SRT); The average time needed for the solid to be held in the digestion process till the gas production ceased is Biological Solid Retention Time (SRT). The performance of a microbial community growing in an AD 2.4.5 system is determined primarily by SRT (Xinyuan, 2010).

Organic Loading Rate; The organic loading rate (OLR) determines the volatile solids input to the digester. It is a measure of the biological conversion capacity of the anaerobic digester system, which has a significant influence on the AD process performance. OLR is stated as the amountin kg of organic matter (as VS or COD) per reactor size. Loading rate plays a vital role in anaerobic wastewater treatment. An excess fed of biodegradable matter to the digester leads to the overproduction of volatile fatty acids, a pH drop and hence a reduction in methane production will occur. When the loading rate is lower the reactor could also lead to decrease in the digester performance due to the scarcity of the nutrients for microbial growth (Isaac, 2003).

Higher OLR needs more of the bacteria, this in turn cause the system to crash if it is not prepared. The short-come of increasing the OLR would be that the acidogenic bacteria, which act early in the digestion process and reproduce rapidly given ample substrate, would multiply and produce acids quickly (Singh, 1974). The methanogenic bacteria, which take longer to increase their populations, would not be able to consume the acids at the same speed. The pH of the system would then fall due to the accumulation of fatty acids, killing more of the methanogenic bacteria and leading to a positive feedback loop, eventually halting digestion. Lowered biogas production and eventually a lower pH is an early clue of high OLR (Vlyssides and Karlis, 2003). The designs of AD mainly depend on loading rates particularly important control parameter in continuous systems.

Table 1: Parameters influencing biogas production

Parameter	Measurement Method	Reference
Cobalt concentration in the high presence of iron concentrations	Total reflection X-ray fluorescence spectroscopy	[9]
VOCs (volatile organic compounds) emitted fromdifferent units of food waste anaerobic digestion plant	Portable GC-MS(gas chromatography–mass spectroscopy)	[10]
H_2S in biogas	Gas responsive nano-switch (copper oxide composite	[11]
CH_4 emissions from pressure relief valves of an agricultural biogas plant	Flow velocity and temperature sensors	[12]
Ammonia in biomethane	Luminescent ammonia sensor based on an imidazole-containing Ru(II) polypyridyl complex immobilized on silica microsphere	[13]
pH, temperature, oxidation-reduction potential (ORP)	via electrodes, on-line monitoring with PCL	[14]
CO_2 , CH_4 , H_2O	On-line monitoring with a Super continuum laser-based off-resonant broadband photo acoustic spectroscopy	[15]
Different volatile fatty acids	On-line monitoring with total-reflectance Fourier-transformed infrared spectroscopy (ATR-MIR-FTIR and XRD)	[16]

Percentage of Solids; AD of organics will proceed best if the feedstock consists of roughly 8 % solids. In the case of fresh cow manure, this is the equivalent of dilution with roughly an equal quantity of water. AD is practiced in two broad categories of solid content: "dry digestion," with typical dry solids content of 25-30% and "wet digestion," with dry solids content of less than 15% (Xinyuan, 2010).

A higher TS contents leads to smaller and thus less costly, reactors. This price savings may be offset, however, by the more expensive pumps needed to move denser material. Higher TS values cause excessive resistance to flow in pipes as well (Nichols, 2004). Systems with lower TS tend to have much better mixing, thus increasing the degree of digestion because the bacteria can more easily access liquid substrate and because the relevant reactions require water. An additional benefit to lower solids content is completemixing of the substrate (Xinyuan, 2010).

Toxic Substances; When planning and operating a biogas plant, it needs to be kept in mind that some compounds inhibit the anaerobic process and can even be toxic at higher concentrations. Generally speaking, the inhibition depends on the concentration of the inhibitors, the composition of the substrate and the adaptation of the bacteria to the inhibitor. Deublein & Steinhauser (2011) listed the following anaerobic process inhibitors: Oxygen, hydrogen sulfide (H_2S), organic acids, free ammonia, heavy metals, tannins and others such as disinfectants (from hospitals or industry), herbicides, insecticides (from agriculture, market, gardens, households) and antibiotics.

Agitation/mixing; The way in which materials flow through the digester impacts the degree of contact substrate has with resident bacteria and therefore how quickly it is digested. In the earliest systems, such as covered lagoons, the feedstock simply sits in a large bath and decomposes without mixing. Enhancements on this system focused on changing the way materials flow, such as in complete mix digesters and plug-flow digesters, or in the way materials are mixed, such as through agitation, gas injection, or recirculation. Mixing can take place as a result of the pathway the waste must travel before it is removed. Some systems have interior walls in a cylindrical chamber that require a greater distance traveled for the waste, thereby increasing mixing (Davis and Cornwell, 1998).

The material inside any digester may be further mixed through mechanical or gas mixers that keep the solids in suspension. Often biogas is bubbled through the chamber as an inexpensive way to promote movement. Recirculating digested waste continuously through heat exchangers both improves mixing and ensures proper temperature control. Mechanical mixers inside digesters are less common because maintenance is extremely difficult. Sealed digesters must be shut down in order to access interior machinery. Mixing can also be achieved through the recirculation of waste. Once digestate is removed from the digester after the gas production ceased, a percentage of it is fed into the stream of incoming fresh waste. This serves to inoculate the fresh waste with bacteria and increase movement in the chamber, which prevents the buildup of a scum layer.

The purpose of mixing in a digester is to blend the fresh material with digestive containing microbes. Furthermore, mixing prevents scum formation and avoids temperature gradients within the digester. However excessive mixing can disrupt the microbes so slow mixing is preferred. The kind of mixing equipment and amount of mixing varies with the type of reactor and the solids content in the digester (Verma, 2002).

Inoculum/Starter; Yaobo *et a*l., (2006) revealed that in order to start up a new anaerobic process, it is critical to use inoculums/ starter for microorganisms to commence the fermentation process, as the growth rates of anaerobic microorganisms is slow, particularly methanogens. The common seeding materials include digested sludge from a running biogas plant or material from well-rotted manure pit or cow manure slurry.

Feedstock; The most important initial issue when considering the application of anaerobic digestion systems is the feedstock to the process. Almost any organic material can be processed with anaerobic digestion; however, if biogas production is the aim, the level of putrescibility is the key factor in its successful application. The more putrescible (digestible) the material, the higher the gas yields possible from the system. As greater cost and impending depletion of fossil fuels became apparent in the 1970's and early 1980's the search for renewable alternative fuels resulted in an expanded interest in anaerobic digestion to include industrial waste (Switzenbaum, 1991), municipal solid waste (Cechi *et al.*, 1993), and biomass energy crops (Chynoweth and Isaac, 1987) as feedstock (Verma, 2004).

Solid waste disposal on land; Wastewater handling (industrial and domestic wastewater); and waste incinerator of fossil based products such as plastics. The highest GHGs emitted from these waste is CH_4 while N_2O only is only emitted in small amount from human sewage and waste incinerator. Solid waste from landfills will emit CH_4 due to the decomposition of organic waste under anaerobic condition and its contribution to the global CH_4 emission was between 5 and 20% (USEPA, 1994; IPCC, 1992). The amount of methane produced depends on the management of the disposed municipal solid waste and the depth of the solid waste in the landfill, therefore, knowledge of the extent and type of active landfill site management is also important.

Achieving the ultimate objective of the UNFCCC needs the involvement of all Parties in decreasing GHG emissions and increasing sinks. In the period of 1990-1995, it has been noted that there is an overall increasing trend of GHG emissions in Ethiopia and it is expected to increase in the future along with socio-economic development and population growth. On the other hand, the sink capacity of the country in the LUCF sector is decreasing rapidly because of deforestation mainly for energy use and agricultural (Abebe Tadege, 2001).

The country is also concerned with the protection of local and global environment. As shown in the 1994 Environmental Policy, Ethiopia is dedicated to work with the international community to combat anthropogenic climate change (Abebe Tadege, 2001). A number of opportunities which could have the indistinguishable objectives of sustainable economic development and GHG mitigation are identified in the Energy, Land Use Change and Forestry, Agriculture and Waste sectors (Abebe Tadege, 2001). Moreover, cost effective technologies like AD are highly recommended to manage waste and mitigating GHG (methane) which have 21 times GWP than CO_2 (Wilkie, 2008; Kruger *et al.,* 2000; IPCC, 1996).

Chapter Three

Materials and Methods

3.1 Materials

Analytical grade chemicals and solvents were used in the study. The chemicals used were sulfuric acid (H_2SO_4), potassium hydroxide (KOH), sodium hydroxide (NaOH), methanol, hydrochloric acid (HCl), hydrogen peroxide, potassium sulfate, boric acid, sand and copper sulfate where i got this from AAIT,5 Kilo campus laboratory The apparatus and materials used in the study were gas kit maker, rubber hose, umber glass bottle, hose, incubator, furnace, measuring cylinder, analytical balance, scissors, stirrer, beakers, desiccators, iron wire, iron rings and standings, clamps, crucible, hot plate, plastic bags, stopper, controlling valves burettes, pipettes, pH meter, conductivity meter, thermometer, filtration flask, funnel and instruments such as spectrophotometer, gas analyzer (Geotechnical instruments UK Ltd). All apparatus/ materials were properly washed with soap solution and allowed to dry by standing over night in the laboratory.

3.2. Feedstock sample collection and Sample Preparation

The feed stocks used for the study were tannery flesh waste, water hyacinth.

Tannery solid waste (skin and trimming) were collected from Abyssinia tannery Share Company, which is found in Addis Ababa the tannery solid waste is processed by cutting and chopping by the knife into small size to increase the surface area of the substrate (tannery solid waste) was

Cow dung as inoculum- was obtained from private dairy farm at vicinity of Saristown which is found in AddisAbaba 10kg of cow dung was collected.

Water Hyacinth (WH)-was collected in Zuway Pond, All the feed stocks were kept at at4^{o}C in refrigerator at the Center of the Environmental Science, until used in digester for biogas production.

3.3 Physico-chemical characterization of the Feedstock

The feasibility of tannery waste as feedstock for biogas production was confirmed for its total solid, volatile solid, carbon and nitrogen contents.

3.4 Total Solid (TS)

Freshly collected cow dung, water hyacinth and tannery wastewater and the pre-treated tannery solid waste were added to crucibles and weighed using analytical balance. A triplicate of five gram of each samples for precision of data were taken and weighed carefully. The weighed samples were then placed inside the oven maintained at about 105^{o}C for 24 hours. A desiccator was used for cooling the sample to room temperature without absorbing the moisture. Finally, the cooled sample was weighed.

The percentage of the total solid of sample was calculated as follow;

$$\%Total\ soild = \frac{C-A}{B-A} x100\% \qquad (1)$$

Where A = Weight of crucible, B= Weight of fresh sample + crucible, C = Weight of dried sample + crucible

3.5.2 Volatile Solid (VS)

Volatile solid is the content that is the lost mass on ignition of the raw waste samples. The total solid (TS) of the oven dried sample was changed to char by combusting it using hot plate for about fifteen to thirty minute and ignited using muffle furnace at 550^{o}C for five hours to determine the volatile solid content of the feedstock sample. The volatile solid in percent was then determined as follows,

$$\%\text{Volatile solid} = \frac{\text{D}-\text{A}}{\text{C}-\text{A}} \text{X}100\% \qquad (2)$$

Where A = Weight of crucible, C = Weight of sample after oven + crucible, D = Weight of sample after furnace + crucible

3.5.3 Fixed Solid/Ash content

The ash that was obtained after ignition of the total solid in muffle furnace is fixed solid. Total solid is the sum of volatile solid and fixed solid (APHA 20e 2540 G, 1999).

3.5.4 Organic Carbon Content

The carbon content of the feedstock sample is estimated from the volatile solid content of the sample. The following formula can be applied to calculate the percentage composition of the carbon content of the sample (Adams *et al.*, 1951).

$$\%carbon = \frac{\%volatile\ solid}{1.8} x100\% \qquad (3)$$

3.5.5 Total Nitrogen

Total nitrogen content of the samples was determined by Kjeldahl method. The procedureis based on the principle that the organic matter is oxidized by treating organic materials with concentrated sulfuric acid, nitrogen in the organic nitrogenous compounds are being converted into ammonium sulfate during the oxidation. Ammonium in the digestate is trapped by the acids which are liberated in the form of ammonia by distilling with NaOH. The liberated NH_3 is absorbed in boric acid and titrated against standard H_2SO_4 or HCl or trapped by standard H_2SO_4 and the excess acid back titrated against standard NaOH solution of the same concentration with the acid used for trapping.

Potassium sulfate is added to raise the boiling point of the mixture during digestion and copper sulfate and selenium powder mixture is added as a catalyst for speeding up the digestion (hastening the reaction). The procedure determines all the soil nitrogen (including adsorbed NH_4^+) except nitrates. The method of determination involves three successive phases, which are; digestion of the organic material (to convert organic N into mineral N form, NH_4^+), distillation of the released ammonium into an absorbing surface or medium, and volumetric analysis of NH_3 formed during digestion process. The detail steps of the processes are stated as follows:

One gram of dried sample of cow dung, water hyacinth and tannery solid waste and tannery wastewater and the slurry of all the digesters after completion of biogas production were taken and placed in a digestion tube and 15 mL of concentrated sulfuric acid (H_2SO_4) was added. Upon this ten gram of potassium sulfate was added to the tube as a catalyst to raise the boiling point of sulfuric acid to the optimum digestion temperature (370°C) and placed in block heater where they were heated at 370°Cfor 90 minutes. Sodium hydroxide was then added to the digestate in order to change ammonium ions to ammonia, and the total available nitrogen was separated by distilling the ammonia and collecting the distillate in 0.18 N (normal) H_2SO_4 solutions. The amount of nitrogen in the condensate was determined by titrating ammonia with a standard solution of 0.1 N NaOH in the presence of methyl red indicator in 0.1 N H_2SO_4 solutions (APHA, 1999). Finally the amount of nitrogen in the sample was calculated using the following formula;

$$\%\text{N in the feedstock} = \frac{(\text{VA}-\text{VB})\text{xNx}0.014\text{xMCFx}100}{\text{w}} \qquad (4)$$

Where, VA = Volume in ml of standard acid used for sample titration,MCF = Moisture correction factor, VB = Volume in ml of standard acid used for blank titration,W = Air dry weight of sample in gram, N = Normality of standard acid used for titration.

3.5.6 Carbon to Nitrogen ratio

Once the percentage of carbon and nitrogen content of the feedstock were determined the carbon to nitrogen ratio (C/N) is calculated by dividing the % carbon to % nitrogen.
Another study by Nagamani and Ramasamy (1999) witnessed that the optimum production of biogas was perceived at TS of 8%. Therefore, to keep the % TS at eight, tap water was used. The amount of water added was determined by the following formula.

3.5.7 Nitrate-Nitrogen (NO3-) Total Phosphate analysis

It is determined calorimetrically using spectrophotometer (DR/2010 HACH, Loveland, USA) according to HACH instructions. Percent of removal efficiency (% RE) for each parameter was determined by the following

$$\%RE = \frac{Ci-Cf}{Ci}\text{x}100 \qquad (6)$$

Where: C_i-Initial parameter concentrationC_f-final parameter concentration

3.6 Digester Compositions

The composition of the digester for this bench scale study was the following:

3.6.1 Feedstock

The feedstock for the study was the tannery waste (wastewater and solid waste and cow dung in different proportion for the evaluation of biogas produced. The amount of TS used in all triplicate treatment was fixed to 100 g by taking the volume of the digester into consideration. Ituen et al. (2007) reported that the percentage of the feedstock total solid in the digester is very essential for efficient biogas production. That is total solid of 8% produce high quality of biogas. Another study by Nagamani and Ramasamy (1999) witnessed that the optimum production of biogas was perceived at TS of8%. Therefore, to keep the % TS at eight, tannery waste water was

used. The amount of water added was determined by the following formula.
Mass of Water added = 8% - mass of feedstock in digester. (7)

$$fm = Tm/TS \tag{8}$$

Where, Fm = feedstock mass poured to the digester, Tm = Total solid poured to the digester (proportion of TS)

Thus, different proportions of tannery waste and cow dung were mixed and poured to the each digester. Anaerobic digesters was prepared in Research Laboratory of Center for Environmental Science; Addis Addis Ababa University. Amber bottles of 2.8 L holding capacity was used as anaerobic digester. The amount of water added will be determined by the following formula. Therefore, for different proportions of tannery solid waste and water hyacinth the amount of water added was calculated using the above formula keeping the total volume to 1.25 L. Giving attention to the total volume of digestate, the amount of the TS used was fixed to 100 g for all the triplicates of the treatments. The mass of pretreated tannery solid waste, water hyacinth and cow dung will be measured and poured to 2.8L digesters. The amount weighed will be calculated by using the above formula. Thus, different proportions of tannery solid waste and cow manure, water hyacinth were mixed and poured into the each digester.

Figure 2: Laboratory scale Anaerobic Digester

3.7 Experimental Design

For analyzing the laboratory results, Design expert version 11 softwer was used. It is a targeted software tool for analyzing and optimization of laboratory experiments. The methodology used was the response Surface methodology (RSM). It is used to analyze the interaction effects between parameters. It is a popular method used for optimization in different experimental designs and processes. RSM implements different designs such as Box-Behnken design (BBD), fully factorial design (FFD), and central composite design (CCD) (Yolmeh & Jafari, 2017). From different types of RSM, Box-Behnken design (BBD) is a second-order response experiment that is more precise and time-saving to apply. BBD is easy to get large experimental trials within few runs. Total numbers of the run are determined by: And based on the equation of Box Benken Design for three central replication number of runs are fifteen. Relation between dependent and independent can be determined by following equation for three factors and second order polynomial.

$$N = K_2 + K + C_p \qquad (9)$$

Where: N is the number of runs, K selective factors, and Cp is the central replication point (Kassahun et al., 2017).

Biogas production potential and quality of the gas produced were evaluated at three different operational treatment using bench scale digester. In the experiment, three different operational parameters are was used (amount of water hyacinth, amount of tannery waste and temperature of specification). A total of 27 combination of anaerobic digesters experiments were generated but using surface response method of Box Behnken Design (BBD) reduced into 15 run using three central run. As referred in reference section three operational parameters were selected for testing based on the objective of the research and their effect on efficiency of bio gas production. Those operational parameters were retention time, mas of water hyacinth and tanner flesh waste. Those parameter are selected depends on the amount of methane.the production of methane was increased on this proportion according to the other research.

Table 2: Selected operational parameters and testing value

Factors	Point of test		
	Low point	Mid-point	High point
Water Hyacinth in g (X_1)	25kg	50kg	75kg
Tannery Flesh waste in g (X_2)	25kg	50kg	75kg
Retention time in day (X_3)	10kg	25kg	40kg

.

Subsequently, for the preparations of feedstock in the above proportion, tap water and inoculum using cow dung taken from operating biogas plant was added and mixed thoroughly. The digesters were assembled in bench scale and sealed properly to protect any leakage. Follow up and data collections were done regularly; temperaturewas measured daily; pH and biogas were measured in 15 days interval while biogas quality was measured weekly.

Table 3: Experimental Design for biogas yield measurement

Run	**Water Hyacinth(g)**	**Tanner flesh waste (g)**	**Retention time (day)**
1	50	25	25
2	50	25	25
3	75	50	10
4	25	75	10
5	25	50	25
6	50	75	40
7	25	25	25
8	50	50	40
9	25	50	10
10	75	50	10
11	50	75	40
12	50	50	25
13	50	50	25
14	75	25	40
15	75	75	25

3.8 Experimental Setup

Piorer to the experiments, all the materials were prepared in size and amount. Water hyacinth were chopped to uniform size of 2cm and tannery flesh waste was size uniformly into 2cm, the cow dung died and using crushed in boil mill crusher to uniform 1mm sieve size. Then using agitating mixer 500g of cow dung were mixed with 1.2 liter of tap water gently for 30 minutes. Theis is followed by measuring the amount of water hyacinth and tannery flesh according to runs in table above and prepared cow dung solution was mixed all together for 10minuts. The pH of the solution was adjusted to 7 using 0.1N of NaOH and HCl (Dar & Phutela, 2017).

3.8.1Anaerobic Digester

The laboratory anaerobic digesters were prepared in the Research Laboratory. Amber bottles of 2.8 L holding capacity will be used as a bench scale digester. To create the anaerobic condition, the bottles will be covered by rubber stopper having two outlets and sealed with gas kit maker so that it is confidently air tight. One gas pipe of 8 mm internal diameter of 0.5 m and 1 m length was immersed to the digester, where the 0.5 m long hose was stretched up to the bottom of solution to measure the pH of the slurry while the second one above the slurry was used to off-take the gas from digester for biogas measurement during the anaerobic digestion. A 0.5 m hose was sealed by pipette tip while the 1 m long hose was controlled by valve. The pH of the slurry cause be measured in two- day interval. The temperature of the room was taken daily and the temperature fluctuation was regulated by sand- jacketing the digester and placed in the box prepared by partition for this purpose.

3.8.2 Biogas and its Quality Determination

The amount (quantity) of biog gas from the digesters cause taken to a volumetrically calibrated collector vessel (measuring cylinder) operating by water displacement in two day interval until the gas production will be ceased. First, a tap water filled graduated measuring cylinder was sealed with rubber stopper having two inlets and one outlet. Plastic pipes having non return valves to were used. One of the inlets is used to connect to the digester to collect biogas that displaces the water in the cylinder. The pressure of the biogas produced caused a displacement of the water through a connecting tube from digester. The second inlet with funnel was used to add water while the gas line is open to avoid pressure above the liquid in the cylinder.

The total biogas produced for each treatment will be done by deducting the share of inoculums to know the contribution of each digester. For that matter, the total amount of biogas produced from each digester’s presented by the figure below is the net biogas produced throughout the digestion periods. Quality of biogas (percentage of methane) was measured by biogas analyzer weekly until the gas production ceased. The hose that takes the gas off was directly connected to the calibrated biogas analyzer and the percentage of methane was displayed on the analyzer. Combustibility of the biogas will be also seen by connecting the gas line to Bunsen burner. The figure below shows how the biogas quality was measured by gas analyzer and combustibility of the biogas was checked.

3.8.3 Monitoring parameters of the Operational conditions in Biogas Plants

In general, monitoring parameters of the biogas plants can be classified under three categories: parameters characterizing the process (feedstock type and quantity, biogas production amount and its quality, reactor temperature, dry matter concentration, ammonia concentration, and pH), parameters supplying early detection of instability (VFA, alkalinity, hydrogen concentration, redox potential, and other complex monitoring parameters), and variable process parameters defined by plant operators (OLR and HRT). The monitoring of the biogas plant's operational parameters can be achieved by on-line, at-line, and off-line analyzers. There is an increased interest in the on-line monitoring applications, due to the fast and automated process control.

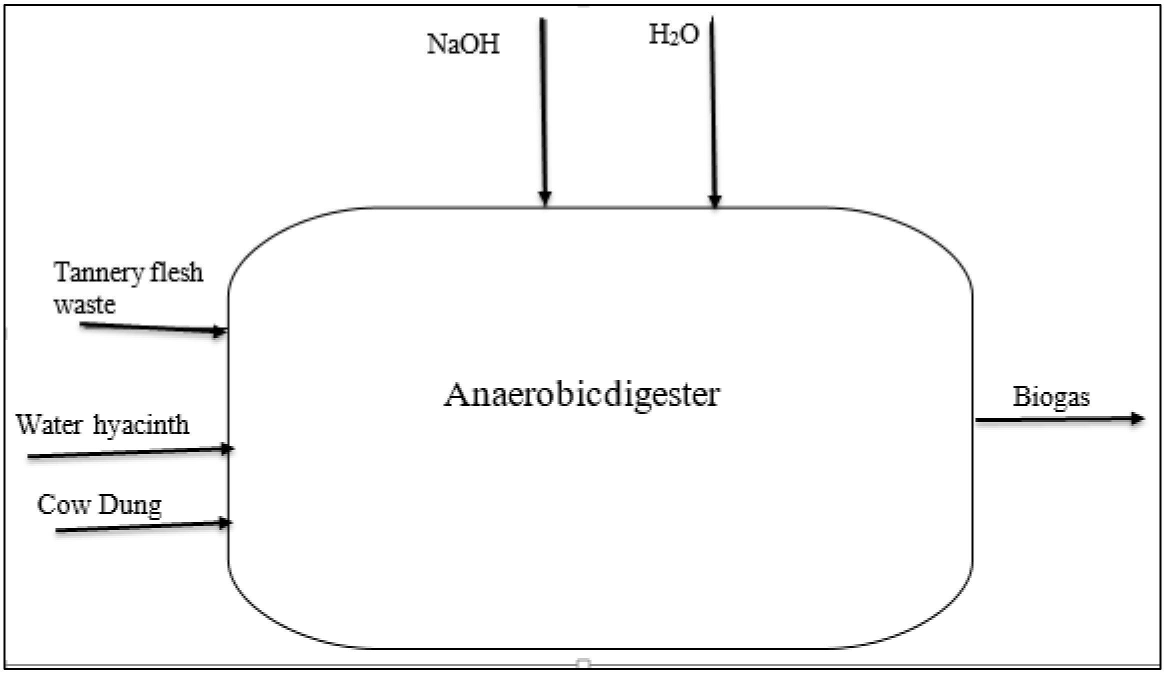

Figure 3: Anaerobic digester operation

3.9 Optimization and Verification of Optimized Operational Parameters

The best optimum operation parameters were estimated using BBD of respond Surface methodology and verified on synthetic wastewater. For three factors and three level of operational parameters the specification criteria of optimization was taken based on specified operations parameter of biogas production. Selected specified operation parameters were; specifying retention time of biogas production in rage of 10 and 30 days. The other specifications were concentration of water hyacinth and tannery flesh waste by mass (in rage of 25 to 75 grams per batch). After optimum operation parameters were determined using statistical software tool of Design-expert, optimum operation parameters were verified in laboratory to evaluate result of determined optimum operation parameters.

3.10 Slurry Analysis

3.10.1Total Solid and Volatile Solid Determination

After the biogas production was ceased the total solid and volatile solid content of the slurries for each treatments were measured to determine the solid reduction (TS and VS). The same methods used for determination of feedstock (section 3.5.1 and 3.5.2).

3.10.2 Sample Analysis

The sample analysis of the samples will be done at different laboratories. Accordingly, COD, TN, TP, S^{2-}, NH^{3-} N, PO_4^{3-} , SO_4^{2-} , and NO_3^- , for tannery solid waste before and after anaerobic digestion, biogas produced, methane content, TS,temperature and pH will be analyzed at Center for the Environmental Science Laboratory; AAU. Volatile solid determination of the feedstocks coas done at laboratory of Center for the Environmental Science and Food and Nutrition Science; AAU.

3.10.3 Data Analysis

For the comparison and report of Physico-chemical parameters of feedstocks, yield and quality of biogas, average values of the triplicate data was used. The collected data was entered to Microsoft Office Excel 2010 and compared and discussed using chat and line graphs.

Chapter Four

Results and Discussion

4.1 Characterization of Feedstock

4.1.1 Characterization of Feedstock in Terms of Biogas Production Parameters

In this study, the TS and VS of feedstock were measured and their average values are tabulated as follows.

Table 4: Characteristics of the Feedstock

Parameters **Feedstock**	**Moisture Content (%)**	**TS (%)**	**VS% on basis of TS**	**Ash % on Basis of TS**	**OC (%)**	**TN (%)**	**C/N ratio**
TSW	43.63	56.37	76.34	23.66	42.41	1.46	29.05
Water Hyacinth	94.80	5.20	61.24	38.76	34.02	0.94	36.19
Cow dung	84.22	15.78	87.67	12.33	49.53	2.74	18.08

The moisture content of tannery solid waste, water hyacinth and cow dung were 43.63%, 94.80% and 84.22%, respectively. The total solid of the feedstock‟s; tannery solid waste, Water Hyaneth and cow dung were 56.37%,5.20 and 15.78%. As it was indicated in the table above tannery solid waste has the highest TS while the wate hyaneth has the lowest TS. For cow dung the total solid obtained in this study was in the range of (15-20%) and comply with the results of Fulford (1988). The TS percentage of each treatment was adjusted to 8% by adding tap water to the digester containing the appropriate amount of the feedstock as the most favorablepercentage of total solids for biogas production is in the range of 8-10% (Jurgen *et al.,* 2001;Ituen *et al.*, 2007).

The volatile solid content of tannery solid waste, water hyacinth and cow dung were 76.34%, 61.24% and 87.67% respectively. The VS as percent of TS in this study for cow dung (87.67%) was almost similar to the value (86.77%) and (86.73%) reported by Ali *et al.*, (2010) and Li et al. (2011), respectively. But it was higher than the value (77%) reported by Fulford (1998). In general, the volatile solid value for each feedstock in this study varies from 61.24%-87.67%, which is within the range of 60% - 87% as reported by Zolar *et al.,* (1998).

Water hyacinth has the least TN and OC while cow dung has the highest TN and OC below. The C/N ratio of the TSW, Water hyacinth and CD was 29.05, 36.19 and 18.08 respectively.Only tannery solid waste has the C/N value in the range of 20-30/1 which is within the recommended range of feedstock to produce the highest/ optimal biogas by Braun (1982). To sum up the C/N ratio of the feedstock for this study is in the range 10–30 as described by Pyle (1978). The variables discussed above are among the main factors that affect the anaerobic digestion processes, the amount and quality of biogas produced. Moreover, the results of the above parameters are also an indication for the feasibility of the feedstock for biogas production. The average C/N ratio of each digester was tabulated below.

Table 5: C/N ratio result of digester

Digesters	D-1	D-2	D-3
C/N	36.19	30	27.32

This is due to the fact that the amount of solid waste that have relatively large percentage (%) of nitrogen increases throughout the treatment compositions.

The carbon to nitrogen ratio obtained from the D-1 = 30:1, D-2 = 27.32:1, D-3 = 29.05 were in agreement with the optimum C/N ratio 20 to 30 as stated by Braun (1982(2001). Quite the reverse, the carbon to nitrogen ratio of D-1 = 36.19, D-2 = 18.23, D-3= 19.49 are beyond the optimum C/N value. For example the C/N ratio of water hyacinth alone is about 36.19 which are greater than the value that can yield optimum biogas but it is below 43 as stated by Stephanopoulos (2007). This shows that tannery solid waste needs a feedstock supplement which is rich in nitrogen.

Fourier Transfer Informed Spectroscopy/FTIR/

Is a technique which is used to obtain infrared spectrum of absorption, emission and photoconductivity of feedstock. The common use is in most cases the identification of unknown materials and confirmation of production materials(incoming and outgoing).

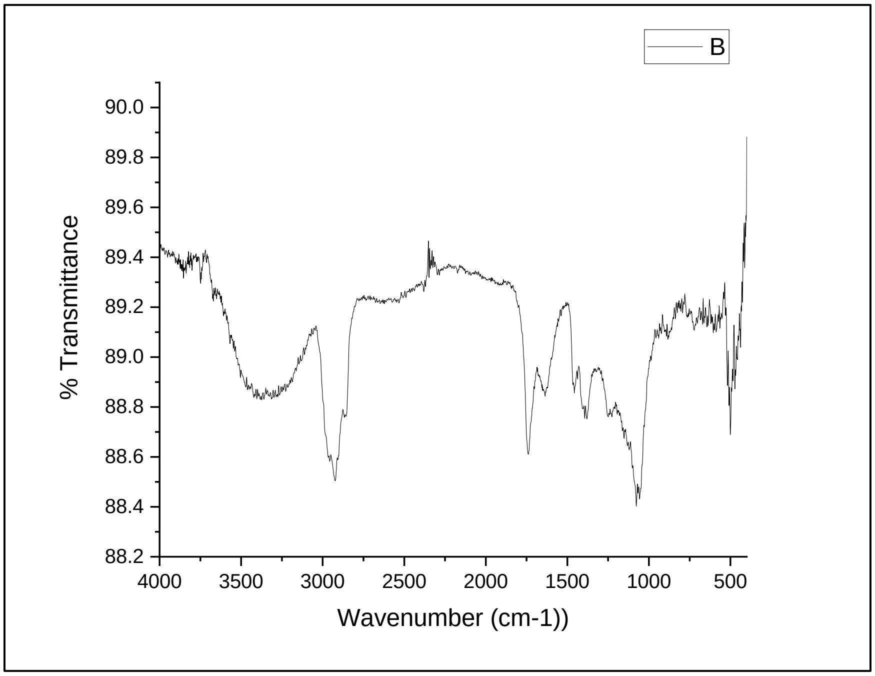

Figure 4: FTIR specification of Tannery Solid waste

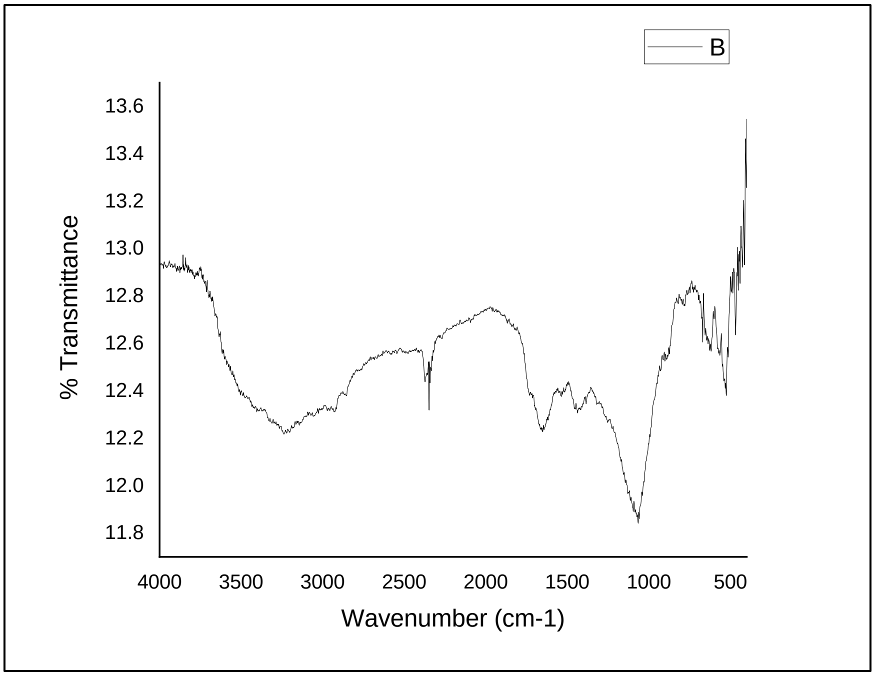

Figure 5: FTIR specification of Water hyacinth

4.1.2 Tannery Wastewater Characteristics before AnaerobicDigestion

Effluents from raw hide and skins processing at Modjo Tannery, which produce crust leather and finished leather, contain COD, TN, TP, S^- , NH_3^- N, PO_4^- , SO_4^- , and NO_3^-. Prior to the start of the bench scale anaerobic digestion of tannery wastewater, the chemical characteristics of the wastewater, used for the anaerobic digestion, was tested for the above parameters. The average COD and TP of the wastewater, which was used for AD, were 6,242 mg/L and 36 mg/L. The average composition of tannery wastewater for the above parameters was summarized in. The average value of tannery wastewater parameters considered in this study are more or less in harmony with the values from the corresponding literatures. The sulfide value of this study is lower because the tannery solid waste used in this study is from general waste line which is a separate channel from the sulfide channel.

Table 6: Tannery Wastewater Characteristics before Anaerobic Digestion and Comparisons with Related Literatures

Parameters	Value	Literature
pH	7	8.63[a],8.2[b]
COD	6142	6.2[c],6.275[a]
TN	784	780[b],760[a]
TP	36	13.75[a]
PO_4^-	8.6	21[c],14[d],15.5[c]
NO_3^-	743	567[a]
NH_3-N	984	563[d]
S^{2-}	96	148.5[a]
SO_4^{2-}	403	502[c],566.7[d]

4.2 The Working Conditions of Anaerobic Digestion Process

Biogas production and its quality were affected by the variables and conditions like temperature, C/N ratio and pH as indicated in section 2.5. The two variables (pH and temperature) were given a consideration for the better biogas production in this study. The outcomes of this study for the two variables (parameters) are given below.

pH

The pH value of all digesting reactors is adjusted to 7 to make it constant factors. The average pH variation of the each digester throughout the reaction period (retention time). It indicates that, the pH value of each digester were dropped in a few days of the reaction time most likely due to organic acid formation which is an indication for the system. The initial values of the pH of the digesters were nearly in the range of the pH values (5.76- 7.12), which is suitable for acidogenic bacteria. These values are in-line with the work of Boopathy and Daniel (1991), which witnessed pH 7 as suitable for acidogenic bacteria to live in. Hence, feedstock with the above pH can be a best input for anaerobic digestion as reported by Monnet . (2003) and Ezoekoye (2009). start up and increase as the methanogenic bacteria consumes the acids produced in the acidogenesis and acetogenesis steps for the production of biogas as stated by Monnet F. (2003).

Decrease in pH is a function of the concentration of volatile fatty acids produced by the activity of hydrolytic acidogenic bacteria capable of degrading the feedstock in the first few days of incubation, bicarbonate alkalinity of the system, and the amount of carbon dioxide produced (Gomec, 2003).

Moreover, the average pH value of D-5 fall as soon as the reaction started may be due to the fat content of the solid waste from the tannery, recovers gradually. Nina *et al.* (2011) verified that, the presence of fat content can raise the formation of VFA, ending in falling of pH. The overall pH of digesters containing tannery solid waste was lower than the digesters containing the other feedstock until the gas production was ceased. The pH of the digesters containing tannery wastewater after a month was almost in the range 6.75–7.11 which can be the main reason for the maximum biogas obtained from D-2, as pH range of 6–7 is very suitable for optimum biogas production due to the normal functioning of methanogenic bacteria in this pH range (Ozmen and Aslanzadeh, 2009). Generally, this laboratory scale experiment has revealed that it is possible to produce biogas from tannery waste co-digested with cow dung in the pH range of 3.96 to 7.11

Temperature

The average room temperature up to two week was fluctuating and then more or less constant until two month and then started to increase up-to the end of the experiment. Moreover, the regression line equation that, the room temperature gradually raise over 80days of retention time. In general, this study revealed the possibility of producing biogas in such ambient temperature range (35-37) by sand-jacketing the digester to control temperature fluctuation, with the cost of retention time of 80 days. A study conducted at ambient temperature by Yitayal (2011) witnessed that; the lower the temperature, the longer the retention time, where in later case was 70 days without water bath.

Amount and Quality of Biogas Produced

The biogas production potential of a feedstock was presented in terms of biogas yield and biogas quality (% methane). The average daily biogas production, the cumulative biogas and the quality of biogas produced by each digester.

Comparison of the Amount of Daily Biogas Produced

The output of the average daily biogas production of each digester for about thirteen week, the rate of average daily biogas production (volume) in almost all digesters increased persistently up to the fifth week and for D-5 and D- 6 the increments continued up-to the seventh week. Maximum and minimum reaction period was recorded 80 and 60 days for D-2 (75% TSW: 25% WH) and D-3 (50%TSW,50%WH) respectively. This is due to the feedstock poor bioavailability though its theoretical biogas yield is high (Steffen *et al.,* 1998). Moreover, the increase of the average daily temperature of the room throughout the reaction can be the reason for the increase of the average daily biogas production, as increase in temperature has a positive effect on biogas yield as indicated by Michael (1979). Most of the biogas was produced during the first five-six weeks of digestion periods; afterwards the biogas production kept decreasing slowly.

4.3 Biogas production

Table 7: Actual and predicted value of biogas yield

Run	Factor 1	Factor 2	Factor 3	Biogas yield/Methane yield	
	A:Water Hyacinth(g)	B:Tannery Flesh (g)	C:Retention Time (Days)	Actual	Predicated
1	25	25	25	71	70.88
2	50	50	25	70	69.67
3	50	75	10	65	65.00
4	50	25	10	68	68.25
5	75	25	25	73	72.88
6	75	50	40	67	67.13
7	50	50	25	70	69.67
8	50	25	40	68	68.00
9	25	50	10	65	64.88
10	75	50	10	72	71.88
11	50	75	40	68	67.75
12	25	75	25	70	70.13
13	75	75	25	70	70.13
14	25	50	40	72	72.13
15	50	50	25	69	69.67

Table 6 show that over all laboratory result of 15 runs and statistical prediction of RSM. The efficiency of biogas production from water hyacinth and tannery flesh waster by using inoculation of cow dung inoculum over all above 60%. Maximum efficiency was obtained at run 5 which mean when the ratio of water hyacinth to tannery flesh waste was 75%:25% and retention time was 25 days. This indicate that the water hyacinth is more efficient than tannery flesh for the production of biogas. And the retention time of 25 days is best time this is because up to 25 days inoculated microbial are adopted the environment and resource for the production of biogas was efficiently available but after 25 days toxic materials are produced and resource scarcity was occurred due to this the production of biogas was reduced. The lowest biogas production result were found at run 3 and run 9 both runs had retention time of 10 days and tannery flesh waste concentration was more concentrated than water hyacinth by 25grams. Which indicate that as tannery flesh was more concentrated and retention time was less and the production of biogas was also less efficient.

Table 8: Three selected biogas production digester to see their effect of time graph

Digesters	**%TS**	**%VS**	**Removal efficiency of %TS**	**Removal efficiency of % VS**
D-1	24.8	33.73	42.27	47.16
D-2	18.5	25.6	57.24	63.03
D-3	18	23	66.51	68.03

4.4 Statically analysis

Statistical method of surface response methodology (SRM) was used for analyzing of laboratory result of biogas production. Using BBD of RSM 15 different laboratory experiment were preformed and to check fit summery, ANOVA result, graph of fitness and 3D graph of operational parameters.

4.4.1 Fitness of Laboratory by RSM

Two fitness were checked, table 7 is summery fit of laboratory result. It show that equation was well fit for generation equation of preformed laboratory result and cubic equation was aliased. Quadratic equation has more well fit R^2 and predicted R^2. The second fit checked was statistical fit, table 8 indicate that the average mean value of laboratory result of biogas production was 69%. The predicted R^2 of 0.93 is reasonable agreement with the adjusted R^2 of 0.96 which has less than 0.2 difference. And adequate precision of 22.88 show that the model can be used to navigate the design space.

Table 9: Fit summary

Source	**Sequential p-value**	**Lack of Fit p-value**	**Adjusted R^2**	**Predicted R^2**	

Linear	0.6303	0.0427	-0.0946	-0.8256	
2FI	0.0695	0.0654	0.3492	-0.9119	
Quadratic	**0.0003**	**0.8576**	**0.9681**	**0.9316**	**Suggested**
Cubic	0.8576		0.9420		Aliased

Table 10: Statistics fit

Std. Dev.	0.4282		**R^2**	0.9886
Mean	69.20		**Adjusted R^2**	0.9681
C.V. %	0.6187		**Predicted R^2**	0.9316
			Adeq Precision	22.8831

4.4.2 ANOVA analysis

Analysis of variance (ANOVA) give us the analysis of selected operation parameters and their nitration effect that their effect were significant or not by evaluating their p and f value. When the P-value is small and F-value is large the effect was more significant. The ANOVA value indicated in table 9 indicate that the mode of laboratory result was significant. The F-value of model was 48.17 and P-value of 0.03% which indicate that the chance of F-value this large could occurred due to noise is too small. When the P-value less than 0.05 the term values are significant this mean A, B, C, their interaction and A^2 and C^2 are significant models of term. The most significant from the term is nitration effect of water hyacinth and retention time. Which show that operational parameter of water hyacinth and retention time has high significant effect on the production of biogas production so it is required to find their optimum operation. The model result show that no lack of fitness of model since 85.76% of chance that lack of fitness occurred. This all indicate that the laboratory result is statistically acceptable.

Table 11: Analysis of Variance for biogas yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	79.48	9	8.83	48.17	0.0003	Significant
A-Water Hyacinth	2.00	1	2.00	10.91	0.0214	
B-Tanner Flesh	6.13	1	6.13	33.41	0.0022	
C-Retention Time	3.13	1	3.13	17.05	0.0091	
AB	1.0000	1	1.0000	5.45	0.0668	
AC	36.00	1	36.00	196.36	< 0.0001	
BC	2.25	1	2.25	12.27	0.0172	
A^2	8.78	1	8.78	47.87	0.0010	
B^2	0.1603	1	0.1603	0.8741	0.3927	
C^2	18.01	1	18.01	98.22	0.0002	
Residual	0.9167	5	0.1833			
Lack of Fit	0.2500	3	0.0833	0.2500	0.8576	not significant
Pure Error	0.6667	2	0.3333			
Cor Total	80.40	14				

4.4.3 Actual Equation of Statistical Model

$$\text{Biogas yield}(\%) = +59.07 + 0.013A - 0.011B + 0.83C - 0.0008AB - 0.008A * C + 0.002BC + 0.002467A^2 - 0.00033B^2 - 0.0098C^2 \qquad (7)$$

Where A represents water hyacinth, B is tannery flesh waste and C stands for retention time. The equation in term of actual factors can be used to make predictions about the response for given levels of each factors. Here the levels should be specified in the original units for each factors. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of center of the design space. The equation is used for prediction or to get result of other value of specified parameters.

4.5 Response Surface Plots

Plots produced in statistical analysis using RSM which used to indicate that predicted and actual runs. They are found fit well and estimate the effect of residual on normal laboratory experimental results. The Normal vs Residual plot, Residual vs predicted plot and predicted vs Actual plot were shown in the figures below.

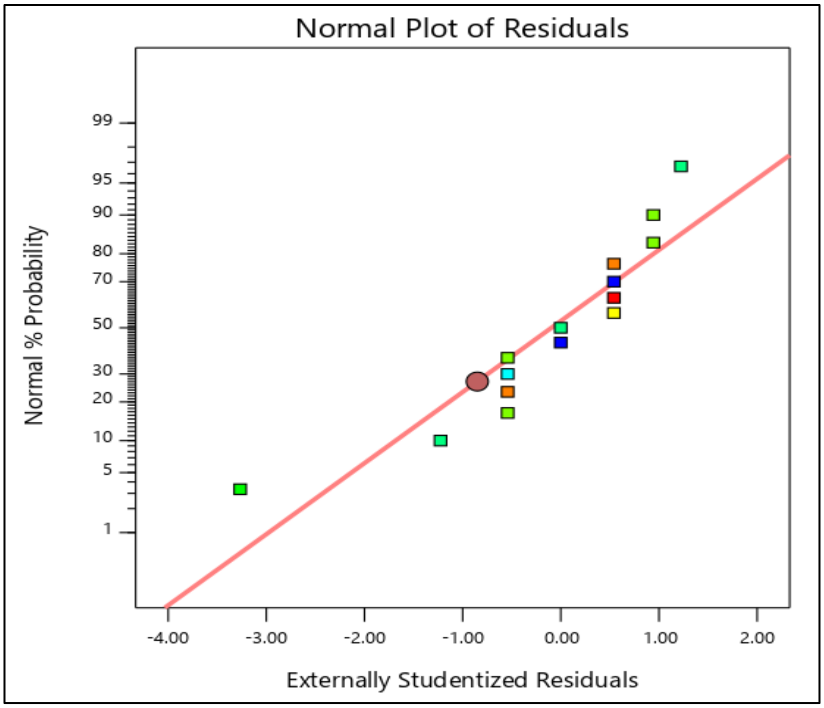

Figure 6: Normal plot of residual

To illustrate more the graphs, figure 10 indicate that normal vs externally residuals it show the effect of residual on normal probability. All the point not much far from diagonal line and it is reasonable acceptable. The next graph is graph of graph of residual vs predicted which indicate that all the point of the graph are in between the maximum and minimum value of graph which show that the graph is acceptable and effect of residual on predicted value is acceptable. The third graph indicated on figure 12 is graph of predicted vs actual run. As shown on table 6 value of actual and predicted are reasonable fit each other and this is proved by their graph to that all the points are lay on diagonal line.

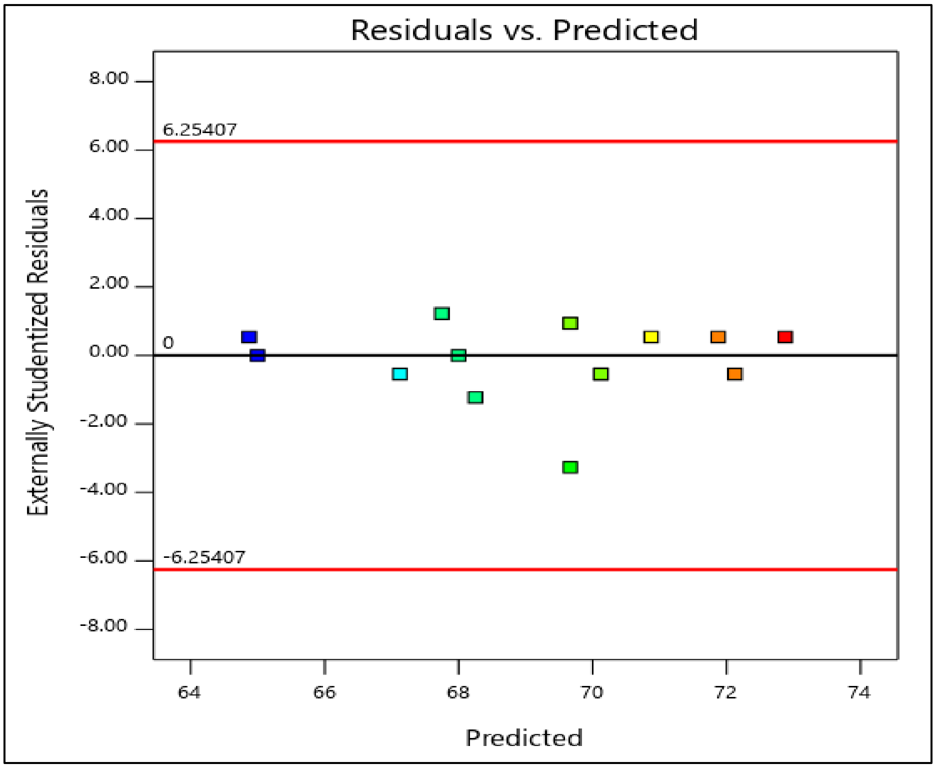

Figure 7: Residue verses predicted plot

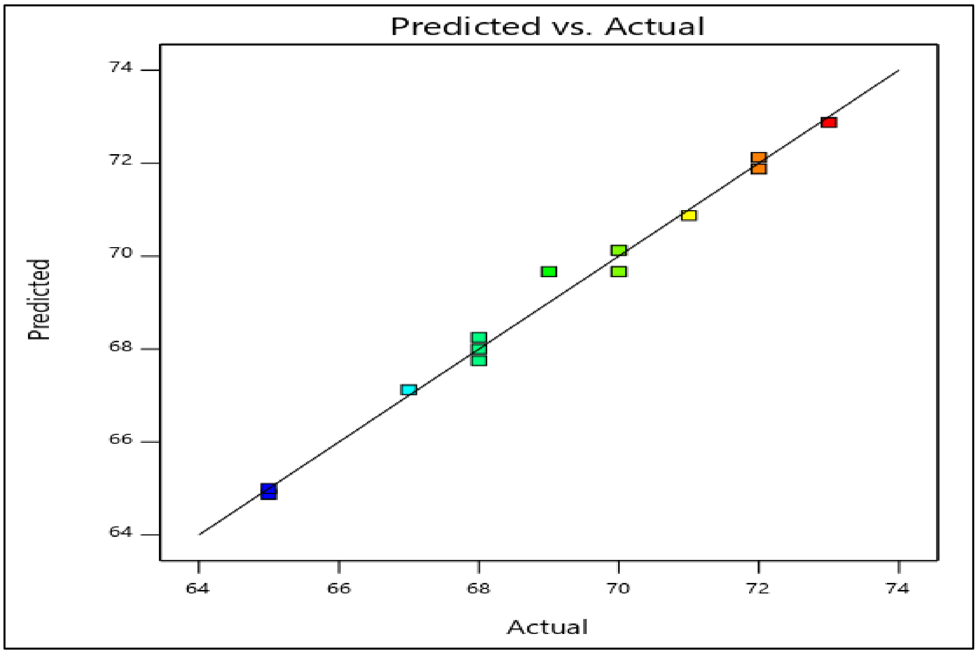

Figure 8: Predicted vs actual plot

4.6 interaction effect of selected operational parameters

As shown in ANOVA table 6 selected operational parapets has interaction effects. Their effects were investigated by keeping on parameters constant and alternatively varying other two operational parameters since quadratic model was used for estimation. Their effect were more illustrated using 3D graph model which shown from figure 13 up to figure 15 blow.

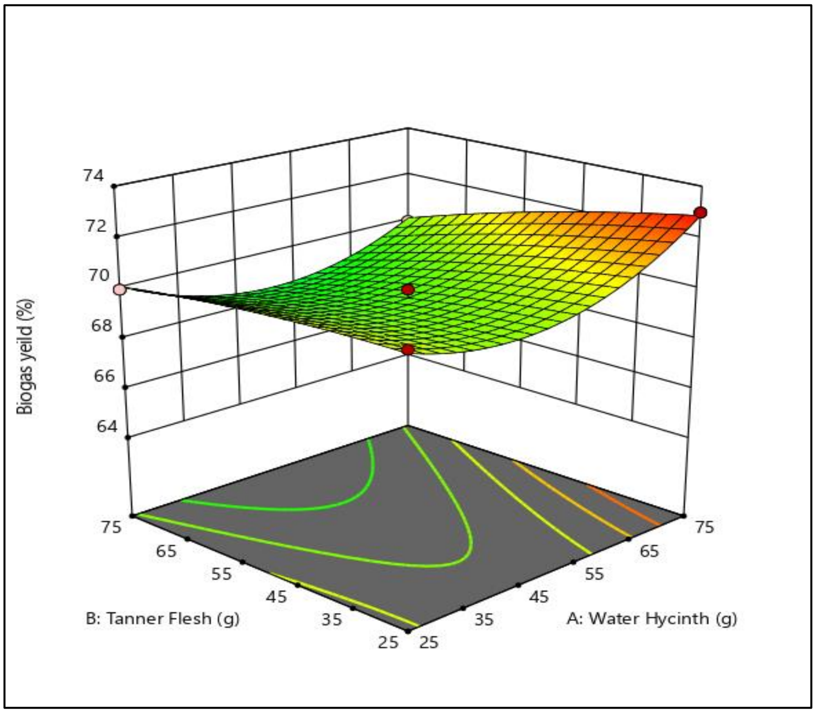

Figure 9: Response Surface plot showing biogas yield (%) up on the variation of tannery flesh and waste hyacinth composition

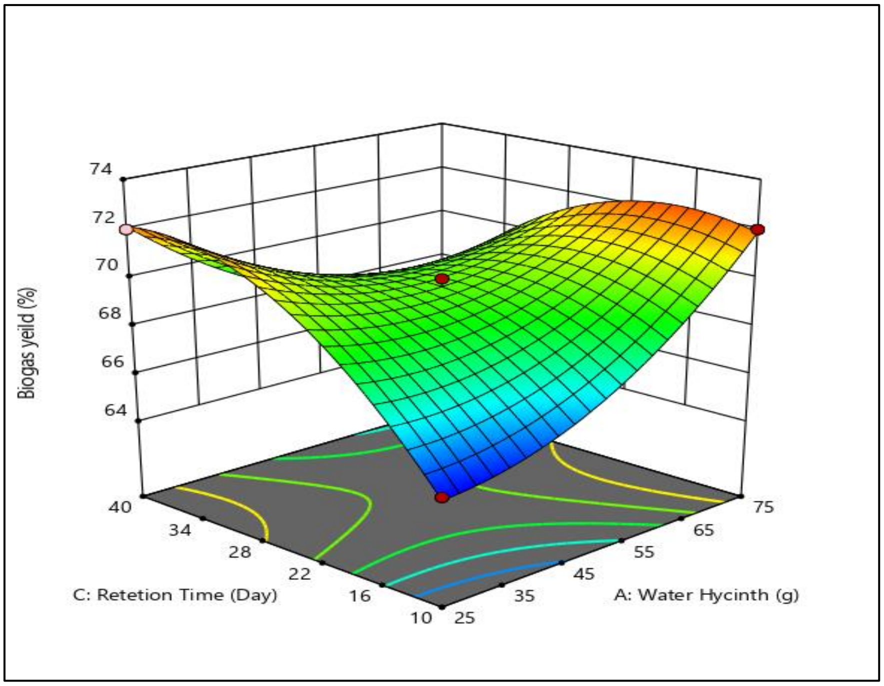

Figure 10: RSM plot showing the Bio gas yield upon the variation of retention time and water hyacinth composition

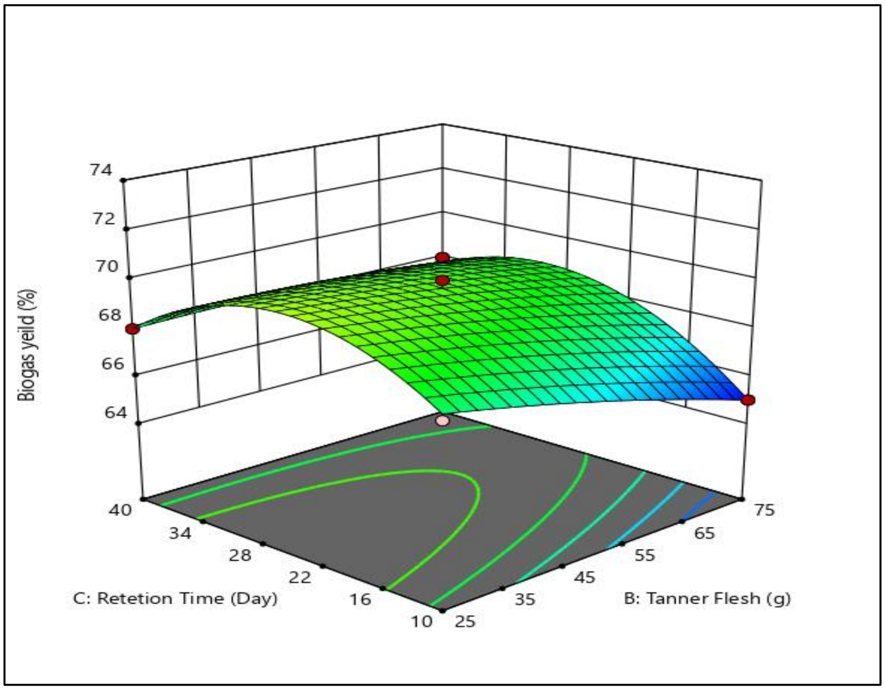

Figure 11: RSM plot showing the biogas yield upon the variation of retention time and tannery flesh composition

As it can be seen from the figure, the rate of average daily biogas production (volume) in almost all digesters increased persistently up to the fifth week and for D-5 and D- 6 the increments continued up-to the seventh week. Maximum and minimum reaction period was recorded 80 and 60 days for D-2 (75% TSW: 25% WH) and D-3 (50%TSW,50%WH) respectively. This is due to the feedstock poor bioavailability though its theoretical biogas yield is high (Steffen *et al.,* 1998). Moreover, the increase of the average daily temperature of the room throughout the reaction can be the reason for the increase of the average daily biogas production, as increase in temperature has a positive effect on biogas yield as indicated by Michael (1979). Most of the biogas was produced during the first five-six weeks of digestion periods; afterwards the biogas production kept decreasing slowly.

The peak value of daily biogas yield in each digester was measured in the range of 36th to 46th days of digestion period; 229, 296, 286mL respectively from D-1 to D-3. The digester containing TSW and WH produced 35-47 % of the total biogas .Moreover, the maximum biogas was produced between the first and nine weeks of the reaction period in all the digesters that was in the range of 100–295 mL. D-1 produces the least biogas until the sixth week of the reaction period while D-2 produce more than others up-to the fifth week. Generally, the daily biogas production in all digester shows the same trend i.e. the biogasproduction was increased up to a maximum and then decreased.

Total Biogas Production

Biogas production was measured for about 13 week of digestion period until gas production was ceased. The total biogas produced during the reaction period for all digester is presented in the figure. The study revealed that, among nine digesters, D-2 produced the highest total biogas (6,535 mL). From the digester containing TSW; the minimum and maximum total biogas was produced by D-1 (4,351 mL) and D-2 (6,535 mL) respectively. Further the results of this study indicate that D-1 was found to produce highest . It is well known that the composition of biogas as well as biogas yields depend on the substrates owing to differences in material characterization in each feed material (Stewart *et al.,* 1984). To sum up D-2 produced the highest biogas within a reaction time of 60 days andD-3 has found to produce the least biogas (2,539 mL) within the shortest RT of 62 days. The other digesters need a week to three weeks additional fermentation period to stop their biogas production.

The average daily biogas production rate can be obtained by dividing the total biogas for the respective RT. Accordingly, D-1, D-2, D3 produced respectively weeks. In addition, depending on the system design and the type of waste feedstock, 55 to 75% of biogas is pure methane (Williams, 1998; Ostrem K., 2004) which is in agreement with the results of this study. Moreover, the combustibility of the biogas produced was tested by connecting the gas line of each digester to the Bunsen burner head. A clear blue flame was observed during the reaction time (Figure 11a-c). As suggested by Curcio *et al.* (2005), the (biogas) mixture of the gases is combustible if its quality (methane content) is more than 50%.

4.6 Characteristics of the Digester after Digestion

4.6.1 Solids Reduction after Anaerobic Digestion

Total solids and volatile solids of the feedstock for all of the digesters after digestion todetermine the amount of solid reduced were analyzed. The total solid and volatile solid of each digesters after digestion period were indicated in the table below.

Anaerobic treatment of wastewater converts the organic pollutants into a small amount of sludge and large amount of biogas (methane and carbon dioxide). Reduction of total solids by 42.27%, 57.24%, 66.51% were observed for digesters D-1 to D-3respectively. High and low removal efficiency of TS (%) was seen for D-2 (75% TWW:25% CD) and D-3 (50%Total Solid Waste,50%Waste Hyacinth).As seen from graph above, reductions in volatile solids 47.16%, 63.03%, 68.03%,were also observed respectively for digesters fromD- 1 to D-3. Similarly, high and low removal efficiency of Volatile Solid was seen for D-2 (75% Tannery Solid Waste: 25%Water Hyacinth).

The highest and lowest solid reduction was recorded for D-2 and D-3 respectively.The relative higher removal efficiency of VS (%) than the TS (%) was a very good indication of high uptake rate of the organic fraction of total solids and the effectiveness of the anaerobic reactor in digesting tannery waste under anaerobic digestion during proper operating conditions.

From the percentage reduction of total solids and volatile solids, it can be put forward that anaerobic digestion can reduce the amount and volume of tannery waste which is disposed in dumpsites. It can also reduce the cost of transport as well as the task of the municipality‟s solid waste management sector.

Comparison of the volatile and total solid before and after digestion gives an indication of the utilization of the organic content in the reactor. Similarly, VS/TS ratio of tannery solid waste before and after digestion was 1.49% and 1.36% respectively. Generally, the ratio of VS/TS before digestion was always relatively higher than the ratio after digestion, which is an indication of the utilization of the organic fraction during the anaerobic digestion; which is true for all the digesters in this study.

6.7 Optimization Result and Verification of Optimum Operation parameters

Statistically obtained optimum parameters was 72.87% efficient with optimum parameters of 75gram water hyacinth and 25gram tannery flesh waste within 25 days. This optimum operation parameter were verified in laboratory having different test and taking the average of the laboratory results. The verification result was 72% efficient which acceptable and verified.

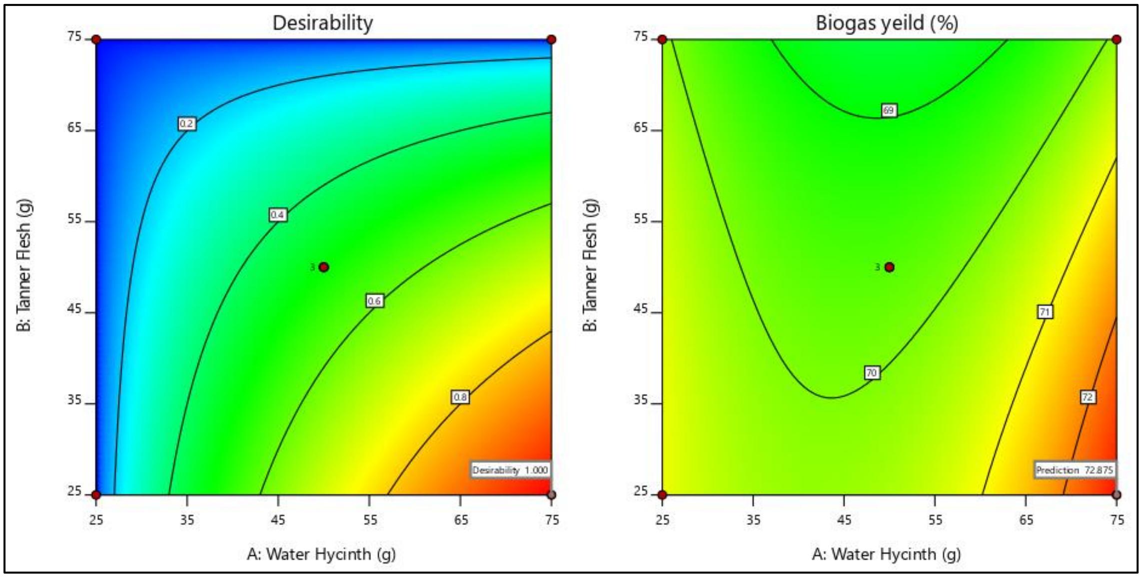

Figure 12: Contour plot showing desirability and Bio gas Yield (%)

Chapter Five

Conclusion and Recommendation

5.1 Conclusion

In conclusion the research on the production of bio gas from anaerobic digestion of water hyacinth and tannery flesh waste using cow dung as inoculum, achieved using three operational parameters and preforming of 15 laboratory experiments. Overall efficiency of biogas produced was 65% and the maximum efficiency was obtained at run 5 which indicated when the ratio of water hyacinth to tannery flesh waste was 75%:25% and retention time was 25 days. From the digesters under this study, those containing tannery solid waste blended with water hyacinth produced the highest biogas volume of 6,537 mL with 73% biogas production quality. Whereas, from the digesters those containing50% TSW, 25%WH blended; produced higher amount of biogas 4,756 mL with 65% quality level. The present research provides an additional benefit of waste management to tannery industries. The results presented here indicate that, anaerobic digestion is a feasible renewable energy and resource recovery option for tannery waste. The research result show that, developing centralized anaerobic digestion for energy and resource recovery from tannery waste is a sustainable and environmentally friendly strategy.

5.2 Recommendation

Based on the study conducted the following points are recommended, the toxicity (effect) level of chromium and sulfide on biogas production of tannery waste should be further studied. Optimization of biogas production from tannery waste at higher temperature 37^{o}C and 55^{o}C mesophilic and thermophilic range should be carried out to see the effect of temperature on both quantity and quality of biogas production.

References

Abdeen M. (2010) Green energy from chemicals and bio-wastes, International Journal for Biotechnology and Molecular Biology Research Vol. 1(7), pp. 101-122, Energy Research Institute, Khartoum, Sudan.

Abebe Tadege (2001) National Meteorological Services Agency, Initial National Communication of Ethiopia to the United Nations Framework Convention on Climate Change (UNFCCC); Addis Ababa, Ethiopia.

Adams, R., MacLean F., Dixon J., Bennett M., Martin G., and Lough R. (1951) The utilization of organic wastes in N.Z.; Second interim report of the inter-departmental committee. New Zealand.

Agunwamba J.C. (2001) "Waste Engineering and Management Tool"; Immaculate Publication Limited, Enugu.

Ahring, M., Angelidaki, I. and Johansen, K. (1992) Anaerobic treatment of manure together with industrial waste; Water Science and Technology vol. 25, pp. 311-318.

Ali, N., Kurchania, A. K and Babel, S. (2010) Bio-methanisation of Jatropha Curcas Defatted Waste Journal of Engineering and Technology Research Vol. 2(3), pp.038-043: Rajasthan, India.

AMCEN Addressing Climate Change Challenges in Africa (2011); A Practical Guide Towards Sustainable Development.

Andualem Mekonnen (2008) Developing a laboratory scale sequencing batch reactor and evaluating its performance for the treatment of tannery wastewater; MSc. Thesis, AAU, Addis Ababa.

Ane S. (2000) Leather tanning in India: Environmental regulations and firms Compliance; F•I•L

Working Papers, No. 21 2000 ISSN 0804-5828.

Anthony, D. C. (1997) Modern Tanning Chemistry, British School of Leather Technology, Nene College of higher education, Boughton Green Road. Mountain Park Northampton, UKNN2 7AL. Chemical Society Review. pp. 111 - 126.

Antonia V. Herzog, Timothy E. Lipman, Jennifer L. Edwards, and Daniel M. Kammen (2001) Renewable energy: A viable choice Published in Environment, Vol. 43 No. 10.

Aslanzadeh, S. and Peyruze, O. (2009) Biogas production from municipal waste mixed with Different portions of orange peel; MSC Thesis University of Boras School of Engineering, Sweden.

Baere, L. (2000) Anaerobic digestion of solid waste: state-of-the-art; Water Science and Technology 41 (3), 283-290.

Barbara H., Horan, Melbourne and Mark, N. (2009) Waste management options to control greenhouse gas emissions Landfill, compost or incineration? F-L Lorecasts and GEOS–Paper for the ISWA Conference, Portugal.

Barnett, A., Leo, P., and Subramanian (1978) Biogas Technology in the Third World: A Multidisciplinary Review.

Bjornsson, L. (2000) Intensification of the biogas process by improved process monitoring and biomass retention; PhD thesis, Department of Biotechnology, Lund University, Sweden.

Bogner, J., M., Abdelrafie Ahmed, C., Diaz, A., Faaij, Q., Gao, S., Hashimoto, K., Mareckova, R., Pipatti, T., Zhang (2007) Waste Management, In Climate Change Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.

Boopathy, R. and Daniels, L. (1991) Effect of PH on Anaerobic Mild Steel Corrosion by Methanogenic Bacteria. Iowa City, University of Iowa.

Braun, R. and Wellinger, A. (2002) Potential of Co- digestion; IEA Bio- energy, Task 37.

Buljan, J., G.Reich, J.Ludvik, (2000) Mass balance in Leather processing; United Nations Industrial Development organization (UNIDO) - US/RAS/92/120.

Cecchi, F., Mata-Alvarez, J., and Pohland, F.G. (1993) Anaerobic Digestion of Solid Waste; Water Science and Technology; Pergamon Press, Oxford. In: Mata-Alvarez J. (Ed.) Bio-methanization of the organic fraction of municipal solid waste, pp.141-179 IWA Publishing.

Charlotte S., Peter K., Emmanuel G. (2009) Greenhouse gases, radiative forcing, global warming potential and waste management – an introduction. Waste Management & Research ISSN 0734–242X, vol. 27: 716–723, DOI: 10.1177/0734242X09345599.

Chynoweth, D. P. and Isaacson, R. (1987) Anaerobic digestion of biomass, Elsevier applied science, London.

Ciborowski, P (2004) Anaerobic Digestion in the Dairy Industry; Minnesota Pollution Control Agency Air Innovations Conference, www.epa.gov.

Cotance (2002) The European Tanning Industry Sustainability Review; World Summit on Sustainable Development.

Curcio, S., Calabro, V., Aversa, M., Ricca, E., Sansonetti, S. and Iorio, G. (2005) Production of Biogas with Bio-conversion of Organic Solid Waste (Manure) and Food Industry Waste; Università Della Calabria

Dar, R. A., & Phutela, U. G. (2017). Optimization of biogas production from water hyacinth (Eichhornia crassipes) Optimization of biogas production from water hyacinth (Eichhornia crassipes). January 2018. https://doi.org/10.31018/jans.v9i4.1489

Dipartimento di Modellistica per l‟Ingegneria Via P. Bucci – Cubo 39/C – 87030 Rende (CS) – ITALY.

Dahlman, J. and Frost, C. (2001) Technologies Demonstrated at Echo; Floating Drum Biogas Digester; Echo, 17391 Durance Rd, USA.

Davis, M. and Cornwell, D. (1998) Introduction to Environmental Engineering.NewYork, WCB/McGraw-Hill.

Demirbas, A. (2003) Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods; a survey Journal of energy conv manages, 44 (13): 2093-2109; Trabzon, Turkey.

Deublein, D., Steinhauser, A. (2011) Biogas from Waste and Renewable Resources. 2nd edition, Wiley-VCH Verlag, Weinheim.

Divakaran, S. (1984) Handbook of Glue and Gelating; Indian Leather, Madras, India.

Drawnel, A. (2008) Increasing of Biogas production at KAPPALA WWTP: Disintegration Method and Laboratory Scale biogas measurement; Royal Institution of Technology, Stokholm.

Durai and Rajasimman (2011) Biological Treatment of tannery wastewater Review; Journal of Environmental Science and Technology 4 (1): 1-17, ISSN 1994-7887.

EEPA (1997) Environmental Protection Authority; Annual Report; Addis Ababa, Ethiopia.

EEPA (2005) Environmental Impact Assessment guideline for tanneries; Addis Ababa, Ethiopia.

Erickson, L.E. & Fung, D. (1988) Handbook on Anaerobic Fermentations; Marcel Dekker, New York. 850p.

Egigu, M. C. (2016). Efficiency of biogas production from cactus fruit peel co-digestion with cow dung co-digestion with cow dung. July.

European Commission, (2011) Joint Research Centre Institute for Prospective Technological Studies

Sustainable Production and Consumption Unit European IPPC Bureau Industrial Emissions Directive

Draft Reference Document on Best Available Techniques for the Tanning of Hides and Skins.

European Commission, Integrated Pollution Prevention and Control (IPPC) (2003) Reference Document on Best Available Techniques for the Tanning of Hides and Skins.

European Union Landfill Directive 1999/31/EC (1999) European Union Publications Office. http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:1999:182:0001:0019:EN :PDF.

Favazzi, A. (2002) Study of the Impact of the Main Policies and Environment Protections Measures in Africa's Leather Industry; Available from: http://www.unido.org/fileadmin/import/10203_StudioFavazzi.4.pdf 4 June 2012.

Fokhrul, M. I. (2009) International Bio-slurry Workshop and Study Tour Prepared for Netherlands Development Organization (SNV), Bangladesh.

Fry, and L.J., Merill (1973) Methane digesters for fuel gas and fertilizer; Newsletter No.3, New Alchemy Institute, Santa Cruz, CA.

Fulford, D. (1988) Running a Biogas Program; a Handbook, Intermediate technology Publications, London.

Garba, B. (1996) Effect of temperature and retention period on biogas production from ligrocellulosic material; Renewable Energy—An Int. J.9 (1–4), 938–941.

Gebren, H.A. and Oelofse, S.H.H (2009) Unlocking the resource potential of organic waste: a South African perspective; Waste Management & Research, 27: 676–684.

Gomec, Y.C., Speece, R.E. (2003) The role of pH in the organic material solubilization of domestic sludge in anaerobic digestion; Water Sci. technol. 48:143-150.

Gotass, H.B. (1956) Composting- Sanitary Disposal and Reclamation of solid Waste; WHO, Geneva, Switzerland.

Hanna Habtemariam (2010) Developing and evaluating the performance of sequencial batch reactor for the treatment of sulfur rich Modjo tannery effulent; MSc. Thesis, AAU, Addis Ababa.

...

Hartmann H. and Ahring BK. (2006) Strategies for the anaerobic digestion of the organicfraction of municipal solid waste: an overview; Water Science and Technology, 53(8):7–22.

Hobson and Palfrey (1996) Control Measures to Limit Methane Emissions from Sewage and Sludge Treatment and Disposal; WRc report DoE 4118, October 1996. Available via the UK DEFRA (DETR).

Isaac A. D. (2003) The potential for the use of up flow anaerobic sludge blanket reactor for the treatment of fecal sludge in Ghana.

Ituen, E.E., John, N.M., Bassey, B.E. (2007) Biogas production from organic waste in Akwa Ibom State of Nigeria. Appropriate Technologies for Environmental Protection in the Developing World, Ghana.

Javed A. C. and Mobeen S. (2000) An assessment of environmental concerns in the leather industry and proposed remedies: a case study of Pakistan Institute of Engineering Sciences and Technology Topi, Dist. Swabi NWFP, Pakistan.

Joshua, R., Ruihong, Z., Bryan, M. and Robert, B. (2008) Current Anaerobic Digestion Technologies Used for Treatment of Municipal Organic Solid Waste. California Integrated Waste Management Board Report, Department of Biological and Agricultural Engineering University of California, Davis.

Jurgen W., Enercess G., and Bad O. (2009) Monitoring of Digester in biogas Plants, German, HACH LANGE.

Kalia V.C., Sonakya V., Raizada N. (2000) Anaerobic digestion of banana stems waste; Bioresource Technol. 73: 191-193.

Kalia, V.C. (2007) Applied Microbiology: Microbial Treatment of Domestic and Industrial Wastes for Bioenergy Production; Institute of Genomics and Integrative Biology, CSIR, Delhi University Campus, Mall Road.

Kalogo, Y., Verstraete, W. (2001) Potentials of anaerobic treatment of domestic sewage under temperate climate conditions; IWA Publishing, pp. 181–203.

Kanagaraj, KC Velappan, NK, Chandra Babu and Sadulla (2006) Solid Wastes Generation in the Leather Industry and its utilization for cleaner Environment; Central Leather Research Institute , Chennai, India.

Kaul, S. N. and Nandy, T. and Vyas, R. D. and Szpyrkowicz, L. (2001) Waste Management in Tanneries: Experience and Outlook. Journal of Indian Association for Environmental Management, 28. pp. 56-76.

Khan,S. R., Khwaja,M.A., Khan, S., Kazmi and Ghani, H. (1999) Environmental impacts and Mitigation Costs of Cloth and Leather Exports from Pakistan, SDPI Monograph Series
M. 12, Islamabad, Pakistan.

Larry E. Erickson, Eric Fayet, Bala K. Kakmanu, Lawrence C. (2004) Anaerobic Digestion. Kansas: National Agricultural Biosociety Center.

Lettinga G., Rebac S., Zeeman G. (2001) Challenge of psychrophilic anaerobic wastewater treatment.Trends in Biotechnology, 19, (9), 363-370.

Li, Y., Park, S.Y., Zhu, J. (2011) Solid-state anaerobic digestion for methane production from organic waste. Renewable and sustainable Energy Reviews 15, 821-826.

Lusk, P. (1999) "Latest Progress in Anaerobic Digestion." Biocycle 40 (7).

Mahlia, T., Abdulmu in, T., Alamsyah, and Mukhlishien, D. (2001) An alternative energy source from palm oil wastes industry for Malaysia and Indonesia; J Energy Conversation and Management, 42: 2109-2118.

Mahony, T., and O'Flaherty, V. (2002) Feasibility Study for Centralized Anaerobic Digestion for the Treatment of Various Wastes and Wastewaters in Sensitive Catchment Areas; Ireland Environmental Protection Agency.

Marchain, U. (1992) Biogas Process for Sustainable Development: MIGAL Galile Technological center Kiryat Shomna, Israel, FAO.

Mata-Alvarez, J. (2003) Biomethanization of the organic fraction of municipal solid wastes; IWA publishing, ISBN: 1 900222 140.

Matteo Carpentieri, Andrea Corti, and Lidia Lombard (2005) Life cycle assessment (LCA) of an integrated biomass gasification combined cycle (IBGCC) with CO_2 removal; Energy Conversion and Management 46 (11-12) 1790-1808.

Mattiasson, B., and Jain, S. (1998) Acclimatization of methanogenic consortia for low pH biomethanation process; biotechnology, vol.20 (8), pp. 771-775.

McCarty, P.L. (1982) In: (D.E. Hughes, D.A. Stafford, B.F. Weatley, W. Beader, G. Lettinga, E.J. Nuns, W. Verstraete and R.L. Wentworth, eds.) Anaerobic digestion. Elsevier Biomedical, Amsterdam, pp. 3- 22. McCoy, J.H. (1962) J. Appl. Bact. 25:213-224.

Mekonnen Bekele and Gezahegn Ayele (2008) The Leather Sector: Growth Strategies through Integrated Value Chain Ethiopian Development Research Institute (EDRI).

Milono P, Lindajati T, Aman S (1981) Biogas production from agricultural organic residues. In the first ASEAN seminar-workshop on Biogas Technology, working group on food waste materials. pp. 52- 65.

Mital, K., (1996) Biogas Systems-Principles and Applications; New age International (P) Ltd.

Monnet F. (2003) An introduction to anaerobic digestion of organic wastes, final report, Remade Scotland.

Mwinyikione M. (2007) Assessment of Anaerobic Lagoons Efficacy in Reducing Toxicity Levels of Tannery Effluent in Kenya; Research Journal of Environmental Toxicology, 1(4): 167-175.

Nagamani, B. and Ramasamy, K. (1999) Biogas production technology; An Indian Perspective Current Science, Vol, 77, No. 641 003.

Nguyen, N. U., Berghold, H. and Schnitzer, H. (2007) Utilization of Agro-Based Industrial by Products for Biogas Production in Vietnam; Proceedings of Asian Power and Energy Systems.

Nichols, C. E. (2004) Overview of Anaerobic Digestion Technologies in Europe, Biocycle 45(1), pp. 47-54.

Nina, K., Miroslav H., Igor, B. and Viera, S. (2011) Utilization of Biodiesel By-Products for biogas Production; Institute of chemical and Environmental Engineering, Faculty of Chemical and food technology, Radlinskeho 9, 812 37 Bratislava, Slovakia.

NRCS (2005) Conservation Practice Standard, Anaerobic Digester in controlled Temperature; Number Code 366.pp 4-5.

Olsen, S., Cole, V., Watanabe, S. and Dean, A. (1954) Estimation of available phosphorus in soils by the extraction with sodium bicarbonate; Circ. 939; U.S. Dep. of Agric.

Omer A. (2010) Sustainable Energy Development and Environment; Research Journal of

Environmental and Earth Sciences 2(2): 55-75, 17 Juniper Court, Forest Road West, Nottingham NG7 4EU, UK.

Ostrem, K. (2004) Greening waste: anaerobic digestion for treating the organic fraction of municipal solid wastes; M.S. thesis in Earth Resources Engineering Department of Earth and Environmental Engineering Fu Foundation of School of Engineering and Applied Science, Columbia University.

Özmen, P. and Aslanzadeh, S. (2009) Biogas production from municipal waste mixed with different portions of orange peel, University of Borås, School of Engineering, Sweden.

P.K. Singh, V. Kumar and S. Singh, (2011) Management of Tannery Waste: Its Use as Planting Medium for Chrysanthemum Plants. Journal of Environmental Science and Technology, 4: 560-567.

Pena-Varo, M.R. (2002) Advance primary treatment of domestic wastewater in tropical countries: Development of high rate anaerobic ponds, Ph.D thesis, Department of civil engineering, university of Leeds, England.

Prakash, C. G. (2008) Training of Trainers (TOT) on Construction and Supervision of SINIDU Model Biogas Plant for Ethiopia Prepared for National Biogas Program (NBP) EREDPC/SNV, Ethiopia.

Pyle, L. (1978) Anaerobic Digestion: Technical Options in Biogas Technology in the Third World. A multidisciplinary review. Ottawa, Ont., IDRC. Pp 50-54.

Qurashi & Tajammul Hussain (2005) Renewable Energy Technologies for Developing Countries Now and to 2023; Publications of the Islamic Educational, Scientific and Cultural Organization ISESCO- 1426A.H.

Rai, G.D. (2004) Non-Conventional Energy Resources, 2nd edition, Khpu Khanna, India. Pp

331-337.

Regional Information Service Centre for South East Asia on Appropriate Technology (RISE-AT) (1998) Review of current status of Anaerobic Digestion Technology for treatment of MSW.

Reijnders, L. and Huijbregts, M.A. (2007) Life Cycle Greenhouse Gas Emissions, Fossil Fuel Demand and Solar Energy Conversion Efficiency in European Bio-Ethanol Production for Automotive Purposes. Journal of Cleaner Production, 15 (18), pp. 1806p-1812.

Saidmamatov, O., Rudenko, I., Baier, U., & Khodjaniyazov, E. (2021). Challenges and Solutions for Biogas Production from Agriculture Waste in the Aral Sea Basin.

Salman Z. (2012) Anaerobic Digestion of Tannery Wastes, Industrial Waste Management, BioEnergy Consult; Powering Clean Energy Future.

Seyoum Leta (2004) Developing and optimization process for biological removal from tannery waste water in Ethiopia; Doctoral dissertation from department of biotechnology,Royal Institute of technology, Stockholm, Sweden. ISBN: 91-7283-8302.

Shealy, J. (2007) A Study on Potentiality of Bio Gas and the Role of the Substrate in Biogas Formation Potential, University of Colorado, Boulder SIT Study Abroud: Mekong Delta, PP20

Shefali V. (2002) Anaerobic digestion of biodegradable organics in municipal solid wastes; Department of Earth & Environmental Engineering (Henry Krumb School of Mines) Fu Foundation School of Engineering & Applied Science Columbia University.

Singh, R.B. (1974) Biogas plant: generating methane from organic wastes; Gobar gas research station, Ajitmal Etawah, p.33.

Song, Z., William, C.J. and Edvyean, R.G. (2001) Coagulation and Anaerobic Digestion of Tannery Waste water; University of Sheffield, UK.

Steffen, R., Szolar, O., & Braun, R. (1998) Feedstocks for anaerobic digestion; Institute of Agro-biotechnology, Vienna.

Stephanopoulos (2007) Challenges in engineering microbes for biofuels production; Science 315(581), pp. 801-804.

Stewart, D.J.; Bogue, M.J.; Badger, D.M. (1984) Biogas production from crops and organic wastes; New Zealand Journal of Science 27(3): 285-294.

Switzenbaum, M.S. (1991) Anaerobic treatment technology for municipal and industrial waters; Water Science and Technology, 24: 281.

Tadesse Alemu (2010) Evaluation of Selected Wetland Plants for the Removal Efficiency of Chromium and Organic Pollutants from Tannery Wastewater in Constructed Wetlands at Modjo Tannery; MSc. Thesis, AAU, Addis Ababa.

Teodorita A. (2007) Promotion of Biogas for Electricity and Heat Production in EU- Countries Economic and Environmental Benefits of Biogas from Centralized Co-digestion Project period: 01.01.2005-30.06.2007 Contract: EIE/04/117/S07.38588.

Thorsten R. and Martin J. (1997) Dissolved organics in tannery wastewaters and their alteration by a combined anaerobic and aerobic treatment; Water Res 31: 1035–1046.

UNIDO (2001) Industrial Environmental Policy and Strategy for Ethiopia; Volume 2(draft), EPA/UNIDO, Addis Ababa, Ethiopia.

US EPA (1994) Characterization of Municipal Solid Waste in the United States; Available at: http://www.epa.gov/osw/nonhaz/municipal/pubs/msw94.pdf.

United Tech, I. (2003) Anaerobic Digestion; UTI Web Design. 2003.

Vasudevan and Ravindran (2007) Biotechnological process for the treatment of fleshing from tannery industries for methane generation; Current science, vol. 93, no. 11, p1494.

Veeken, A., Kalyuzhnyi, S., Scharff, H., and Hamelers, B. (2000) Effect of pH and VFA on hydrolysis of organic solid; Journal of Environmental Engineering, vol. 126 (12), pp. 1076-1081.

Vlyssides, A. G. and P. K. Karlis (2003) Thermal-alkaline solubilization of waste activated sludge as a pre-treatment stage for anaerobic digestion; Bio-resource TechnologyArticle in Press.

WHO (World Health Organization) (2006) Guidelines for the safe use of wastewater, excreta and grey water; use in agriculture; vol. 4, ISBN 92 4 154685 9.
Wilkie A.C. (2008) Bioenergy: Biomethane from biomass, Bio-waste and Biofuel; J.Well et al. Washington DC, pp195-199.

Wilkie, A. C. (2000) Reducing Dairy Manure Odor and Producing Energy, BioCycle, 41(9), pp 48-50.

Williams, P.T. (1998) Waste treatment and disposal; Chichester: John Wiley and Sons.

Yadav L.S.and P.R.Hesse (1981) The development and use of biogas technology in rural areas a status report Improving soil fertility through organic recycling; FAO/UNDP Regional Project RAS/75004.Project field Document No.10.

Yadvika, S., T.R. Sreekrishnan, Kohli S.and Rana V. (2004) Enhancement of biogas production from solid substrates using different techniques a review; Bioresource Technology, India.

Yaobo F., Gang L., Linlin W., Wenbo Y., Chunsong D., Huifang X., and Wei F. (2006) Treatment and reuse of toilet wastewater by an airlift external circulation membrane bioreactor; Process Biochemistry 41 1364–1370. Research Center for Eco- Environmental Sciences, Chinese Academy of Sciences (CAS).

Yitayal Addis (2011) Study on Biogas Energy Production from Leaves of Justicia schimbriana; MSc. Thesis, AAU, Addis Ababa.

Zennaki, B.Z., Zadi, A., Lamini, H., Aubinear, M., Boulif, M. (1996) Methane Fermentation of cattle manure: effects of HRT, temperature & substrate concentration. Tropicultural 14(4), 134–140.

Zolar, S., Steffen, R. and Braun R. (1998) Feed Stocks for Anaerobic Digestion, Institute of Agro-Biotechnology Tullen, University of Agriculture, Vienna.

Appendix

Appendix I: Table of option of optimum conditions

Number	Water Hyacinth(g)	Tanner Flesh(g)	Retention Time(days)	Biogas yield	
1	**75.000**	**25.000**	***25.000***	**72.875**	**Selected**
2	75.000	25.000	*34.381*	70.057	
3	75.000	25.000	*20.319*	73.635	
4	75.000	25.000	*22.294*	73.367	
5	75.000	25.000	*11.580*	73.903	
6	75.000	25.000	*35.801*	69.480	
7	75.000	25.000	*37.477*	68.748	
8	75.000	25.000	*38.291*	68.372	
9	75.000	25.000	*12.982*	73.961	
10	75.000	25.000	*15.999*	73.955	
11	75.000	25.000	*20.458*	73.619	
12	75.000	25.000	*12.339*	73.939	
13	75.000	25.000	*39.596*	67.743	
14	75.000	25.000	*29.171*	71.835	
15	75.000	25.000	*36.158*	69.328	
16	75.000	25.000	*39.264*	67.907	
17	75.000	25.000	*36.985*	68.968	
18	75.000	25.000	*10.157*	73.805	
19	75.000	25.000	*15.698*	73.964	
20	75.000	25.000	*18.917*	73.779	
21	75.000	25.000	*26.203*	72.610	
22	75.000	25.000	*24.025*	73.069	
23	75.000	25.000	*26.842*	72.458	
24	75.000	25.000	*27.125*	72.388	
25	75.000	25.000	*25.836*	72.694	
26	75.000	25.000	*32.969*	70.592	
27	75.000	25.000	*38.834*	68.115	
28	75.000	25.000	*18.423*	73.821	
29	75.000	25.000	*15.225*	73.974	
30	75.000	25.000	*23.041*	73.245	
31	75.000	25.000	*16.790*	73.924	
32	75.000	25.000	*14.735*	73.979	
33	75.000	25.000	*15.021*	73.977	
34	75.000	25.000	*35.346*	69.669	
35	75.000	25.000	*19.822*	73.691	

36	75.000	25.000	*30.721*	71.362	
37	75.000	25.000	*37.806*	68.598	
38	75.000	25.000	*17.740*	73.870	
39	75.000	25.000	*27.687*	72.244	
40	75.000	25.000	*32.576*	70.733	
41	75.000	25.000	*36.455*	69.201	
42	75.000	25.000	*29.776*	71.656	
43	75.000	25.000	*10.973*	73.866	
44	75.000	25.000	*16.415*	73.940	
45	75.000	25.000	*36.031*	69.383	
46	75.000	25.000	*31.832*	70.994	
47	75.000	25.000	*29.607*	71.707	
48	75.000	25.000	*11.420*	73.894	
49	75.000	25.000	*10.009*	73.792	
50	75.000	25.000	*36.597*	69.139	
51	75.000	25.000	*14.901*	73.978	
52	75.000	25.000	*35.099*	69.770	
53	75.000	25.000	*17.321*	73.896	
54	75.000	25.000	*34.665*	69.945	
55	75.000	25.000	*20.752*	73.583	
56	75.000	25.000	*25.655*	72.734	
57	75.000	25.000	*34.316*	70.083	
58	75.000	25.000	*32.683*	70.695	
59	75.000	25.000	*23.699*	73.129	
60	75.000	25.000	*12.792*	73.956	
61	75.000	25.000	*14.613*	73.980	
62	75.000	25.000	*10.286*	73.815	
63	75.000	25.000	*11.102*	73.875	
64	75.000	25.000	*37.248*	68.851	
65	75.000	25.000	*30.192*	71.529	
66	75.000	25.000	*33.625*	70.348	
67	75.000	25.000	*39.917*	67.583	
68	75.000	25.000	*12.520*	73.946	
69	75.000	25.000	*22.032*	73.407	
70	75.000	25.000	*32.293*	70.833	
71	74.999	25.000	*28.761*	71.952	
72	75.000	25.001	*18.211*	73.837	
73	74.997	25.000	*10.460*	73.828	
74	74.921	25.000	*10.001*	73.769	
75	74.764	25.000	*40.000*	67.532	
76	73.955	25.000	*39.999*	67.499	
77	75.000	29.562	*10.000*	73.473	
78	51.854	25.000	*40.000*	67.860	

Appendix II: Over all report of statistical analysis

Run Order	**Actual Value**	**Predicted Value**	**Residual**	**Leverage**	**Internally Studentized Residuals**	**Externally Studentized Residuals**	**Cook's Distance**	**Influence on Fitted Value DFFITS**	**Standard Order**
1	71.00	70.88	0.1250	0.750	0.584	0.541	0.102	0.937	1
2	70.00	69.67	0.3333	0.333	0.953	0.943	0.045	0.667	15
3	65.00	65.00	0.0000	0.750	0.000	0.000	0.000	0.000	10
4	68.00	68.25	-0.2500	0.750	-1.168	-1.225	0.409	-2.121	9
5	73.00	72.88	0.1250	0.750	0.584	0.541	0.102	0.937	2
6	67.00	67.13	-0.1250	0.750	-0.584	-0.541	0.102	-0.937	8
7	70.00	69.67	0.3333	0.333	0.953	0.943	0.045	0.667	14
8	68.00	68.00	0.0000	0.750	0.000	0.000	0.000	0.000	11
9	65.00	64.88	0.1250	0.750	0.584	0.541	0.102	0.937	5
10	72.00	71.88	0.1250	0.750	0.584	0.541	0.102	0.937	6
11	68.00	67.75	0.2500	0.750	1.168	1.225	0.409	2.121	12
12	70.00	70.13	-0.1250	0.750	-0.584	-0.541	0.102	-0.937	3
13	70.00	70.13	-0.1250	0.750	-0.584	-0.541	0.102	-0.937	4
14	72.00	72.13	-0.1250	0.750	-0.584	-0.541	0.102	-0.937	7
15	69.00	69.67	-0.6667	0.333	-1.907	-3.266	0.182	-2.309	13