ANAEROBIC DIGESTION OF TANNERY SOLID WASTE BY MIXING WITH DIFFERENT SUBSTRATES

By

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BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY

March, 2012

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A thesis submitted to the Department of Civil Engineering of Bangladesh University ofEngineering and Technology, Dhaka, in partial fulfillment of the requirements for thedegree of

MASTER OF SCIENCE IN CIVIL AND ENVIRONMENTAL ENGINEERING

Department of Civil Engineering

BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY

March, 2012

The thesis titled **"ANAEROBIC DIGESTION OF TANNERY SOLID WASTE BY MIXING WITH DIFFERENT SUBSTRATES"** submitted by Shilpy Rani Basak, Student No: 100704153 (P), Session: October 2007 has been accepted as satisfactory in partialfulfillment of the requirement for the degree of M.Sc. Engineering (Civil and Environmental) on 10th of March, 2012.

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It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma (except for publication).

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Shilpy Rani Basak

Dedicated
To
My Mother

ACKNOWLEDGEMENT

First of all the author would like to express her deepest gratitude to the most powerful, the gracious creator for giving knowledge, energy and patience to completing the thesis work successfully.

The author wishes to express her deepest gratitude to Dr. Md. Delwar Hossain, Professor, Department of Civil Engineering, BUET and to Dr. Mohammad Abdur Rouf, Principal Scientific Officer, IFRD, BCSIR for their continuous guidance, invaluable suggestions, constructive comments and endless encouragement throughout the research work and the preparation of this thesis.

Contribution of the Institute of fuel research and Development (IFRD), BCSIR, Dhaka by providing laboratory facilities for performing thesis work is highly acknowledged. The author is also grateful to Md. Saiful Islam, Senior Scientific officer, IFRD, BCSIR and the lab assistants of IFRD, BCSIR, whose suggestions and assistance contributed to the thesis.

The author also wishes to express her gratefulness to the all personnel of Environmental Engineering laboratory, BUET, for their total cooperation.

The author is also thankful to Md. Moinul Islam, Leather expert, Lien tannery, for his valuable suggestions and support.

Finally, the author reports with deep admiration, the patience, caring and encouragement had been shown by her mother in law and husband, throughout the period of this study.

ABSTRACT

Leather is one of the most prospective industries in Bangladesh .Out of the total 206 tanneries in Bangladesh 192 of them are located in Hazaribagh of Dhaka city. A large amount of solid waste (even in lean season 69.1 ton/day according to 2006 survey of UNIDO) is generated daily by leather manufacturing process in this area and crude disposal of this waste are creating serious hazard to the environment. An attempt has been made to analyze the present status of Hazaribagh in terms of solid waste management. Now it is prerequisite to develop an appropriate waste management system of the tannery waste and for this it is obvious to manage each fraction of the waste in a cost effective and environment friendly way. With rapid depletion of conventional energy sources, the need to find an alternative, preferably renewable, source of energy from waste is becoming increasingly important for the sustainable development. A major portion of the solid wastes from leather industry is fleshing, originates from animal tissue, which contains mainly fat and protein, and residual chemicals such as lime and sulphide used in the unhairing process of beam house operation.

Experimental results showed that fleshing contains a significant quantity of volatile solids (including non-biodegradable fraction of volatile matter such as lignin, 82.57%VS) amenable for biodegradation. Further the characterization of fleshing showed that it contains low C/N ratio (2.64) and high pH (10.99), these characteristics were not suitable for using fleshing alone as substrate for anaerobic digestion,for this reason different proportion of cowdung and domestic sewage were used as co-substrate for optimum results. The study was carried out by using different proportions of waste fleshing, cowdung and domestic sewage in four different laboratory scale reactors carrying 6% total solid concentration. In all the reactors fleshing and domestic sewage were mixed in 1:1ratio. Anaerobicdigestion was carried out for 60 days of digestion period at room temperature 30°c ±3 and the pH of the slurry was maintained by the process itself. The inoculums were synthesized by the cowdung and water in the laboratory in the same environmental condition taken for the study and sufficient active biomass was present there.For thatthe start-up of the reactor was achieved easily.

The reactors were subjected to anaerobic digestion with an aim of developing an appropriate technology for recovery of bioenergy from the tannery solid waste fleshing. From the study it was observed thatamended fleshing with domestic sewage when mixed with cowdung, the significant increase of gas production was remarkable. The performances of the reactors were analyzed on the basis of volatile solids destruction efficiency, specific gas yield, COD reduction rate and on methane yield. Within four reactors the percentages of volatile solid destruction were between 42% to 52%, specific gas production were 0.401, 0.476, 0.239 and 0.288 l/g respectively according to volatile solids fed and methane yieldwere achieved72%, 73%, 70% and 72% by volume respectively.COD reduction achieved in the test reactors 48.02% 50.67%, 44.80% and 44.61% respectively. Further, the kinetic analysis of the data revealed that first order kinetic model is adequate to describe the co-digestion of animal tissue with cowdung and domestic sewage.

On the basis of analysis of the performance of the reactors, it was evident that amended fleshing is highly potential substrate for biogas generation and it was also found that R2 reactor, where on the total solids (6%TS) of the slurry 75% of fleshing with domestic sewage and 25% of cowdung were used, showed the optimum results in terms of VS reduction (52%), specific gas yield (0.476 l/g) and methane yield (73% by volume). For this reason, the standards of the reactor R2 were chosen as optimum condition for gas generation from fleshing. The criteria of the reactor R2 can be used for further study or design purposes. Based on the principles of R2 reactor, the economic feasibility of a fleshing based pilot scale biogas plant was also studied. The economic return was found to be 3.5 years for that type of plant.

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LIST OF ABBREVIATIONS

AD	Anaerobic Digestion
BFLLFEA	Bangladesh Finished Leather, Leather Goods & Footwear Exporters Association
BOD	Biochemical Oxygen Demand
BTA	Bangladesh Tanners Association
COD	Chemical Oxygen Demand
Conc.	Concentration
EPB	Export promotion Bureau
KVIC	Khadi and village industries commission
Kcal	Kilo Calories
l/g	Liter per gram
mg	Mili gram
ml	Mili litre
m^3	Cubic meter
R1	Reactor one
R2	Reactor Two
R3	Reactor Three
R4	Reactor Four
Temp.	Temperature
TS	Total Solids
UNIDO	United Nations Industrial Development Organization
VS	Volatile Solid
VFA	Volatile Fatty Acid

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Leather and leather products have always been a part of our heritage and after the emergence of an independent Bangladesh in 1971; the industry received a fresh momentum. Bangladesh started exporting crust and finished leather in early 80's and footwear and other manufactured leather goods during 90's. The contribution of leather industrial sector in the past decade was around US$ 250 million per year, accounting for around 3% of the country's export. Leather and leather goods are the third exportable item from Bangladesh according to EPB report. The leather industrial sector of Bangladesh has been almost entirely supportedby local raw material resources. About 40% of the yearly production of cow hides and goat and sheep skins are available during the Qurbani time and processed within the 75 days following the Qurbani (BFLFEA), while the rest of the material is processed during the remaining period of the year. Buffalo hides are available all over the year at a more or less uniform rate. Accordingly the peak load during the Qurbani period (75 days) is estimated at 450 t/day and the load during the rest of the year (225 days), at about 230 t/day (Nemec, 2010). Out of the total 206 tanneries in Bangladesh 192 of them are located in Hazaribagh district of Dhaka city.

The tanning industry of Bangladesh is primarily concentrated in Hazaribagh (25 hectares of land within Dhaka city) as most of the operating tanneries are located there (Rahman, 1984). In the early 1950sHazaribagh was declared as a tannery estate (in 1951) by a Government gazette notification. However, with the rapid growth of the city over the past five decades, now Hazaribagh itself is surrounded by densely populated localities of the city.

The situation in Hazaribagh today can be described as a mixture of hazard and disaster. There is very little consciousness about environmental pollution. The technological standards that have been set up when the industry was established in the 1960s have remained almost unchanged. According to UNIDO(2010) report, on an average about 15,000 $m^3$of highly polluted wastewater generated everyday by tanneries in Hazaribagh area is discharged, untreated, into the open channel drains

along the roadside passing through the area, which then eventually ends up in the Buriganga river. Often, the drains in the area spill over causing a highly unhealthy atmosphere. Due to the chemicals in the water flocculation takes place, which results in the settling of sludge in channels, which consequently need to be cleaned frequently. The extracted sludge is stored on the sides of the streets and roads.

According to Nemec (2010), in lean season 69.1 tons and in peak season 136.6 tons solid waste is generated everyday by the tanneries in Hazaribagh. Solid waste generated during the tanning of hides and skins (trimmings, fleshings, shavings, etc) are simply dumped along the rim of the streets or in opened uninhabited spaces. The part of waste which is not collected or utilized (converted) eventually dries up or drains off to the Burigangariver in the rainy season, creates bad smell, produces methane gas. Moreover, as a result of disposal of waste and wastewaters, the soil in Hazaribagh has received the industrial chemicals for years – it is undoubtedly becomes quite polluted and loses its fertility. There is an elaborate system of collection and reuse established for certain types of tannery effluent (spent chrome liquor) and solid waste (mostly raw trimmings, chrome shavings, leather scraps and pieces). A substantial quantity of waste is converted into usable products even though by very unsophisticated methods. As there is no infrastructure for treatment of solid or liquid waste generated by tanneries, a very unhygienic atmosphere has been created in the entire locality by discharging/disposing of crude solid and liquid wastes. At this stage, Govt. through the High Court, has ruled that the tanneries should relocate to Savar by February 2010. However, this timeline has since proven to be unrealistic; this is mainly because the start of the construction of the CETP has not yet begun, but also because tanneries are not yet ready to move.

But to save the environment as well to save the leather industry it is high time to think about the technological measures to combat environmental challenges from leather processing activities. Some research has been done on liquid fraction of tannery waste but solid waste fraction has been caught less attention in the recent years. Leather manufacturing processes generate solid wastes varying in composition and quantity at various stages (Thangamani et al, 2009). Hence, the solid waste management system of Hazaribagh area requires special attention to reduce environmental degradation.

For developing a proper solid waste management system for the tannery waste, it is obvious to manage each fraction of the waste in a cost effective and environment friendly way. With rapid depletion of conventional energy sources, the need to find an alternative, preferably renewable, source of energy from waste is becoming increasingly important for the sustainable development. A major portion of the solid wastes from leather industry is fleshing which contains mainly fat and protein and residual chemicals such as lime and sulphide used in the unhairing process of beam house operation (Thangamani et al, 2009). Gaseous efficiency of fat is estimated to be higher than those of carbohydrates and proteins therefore lipid rich waste can be regarded as a large potential renewable energy source (Cirne et al, 1982).

It is important to evaluate appropriate technique or technologies for recovering energy from waste. Anaerobic digestion is considered as the one of the best treatment method for organic fraction of the segregated waste. Anaerobic digestion is a microbiological process of decomposition of organic matter, in the absence of Oxygen, which has two main end products: biogas and digestate (Seadi et al, 2008). Anaerobic digestion ensures recovery of energy in the form of biogas which is a clean fuel as compared to other solid or liquid fuel (Thangamani et al, 2009). Digestate is the decomposed substrate, rich in macro- and micro nutrients and therefore suitable to be used as plant fertilizer (Seadi et al, 2008).It occupies very little land and requires low or no energy in operation(Rahman and Muyeed, 2010). In this study the potentiality of biogas production has been investigated using amended tannery solid waste fleshing.

1.2 Scope of the Study

Leather processing industry generates various types of waste in various quantities. Some portion of Solid wastes generated in Hazaribagh reusing for making glue, poultry feed, recovery of fat, fish feed, etc. Some portion is also sold for making belts or other tiny leather goods. All these jobs are not harmful but the way they follow for preparing these are harmful for the environment as well as for their health also.

To draw the picture of present solid waste management status of Hazaribagh a study based on field survey and secondary data has been conducted. In order to examine appropriate technology for the management of solid waste from tanning industry, anaerobic digestion process has been studied using batch reactors. Batch studies have been performed with limed fleshing,an animal tissue waste obtained in the preparatory stages of leather processing in a tannery. Cowdung and domestic sewage has been usedin the digestion process to modify the tannery solid waste fleshings for using as substrate. Due to lack of resources and modern technology not much is being done to improvise the study.

An attempt has been made to develop an appropriate technology for recovery of bioenergy from tannery solid waste. It is highly expected that the information generated from this study will provide the practical knowledge about the biogas production from tannery solid waste fleshings. Success of this research will open a new horizon for tannery solid waste management for Bangladesh.

1.3 Objective of the Study

The overall objective of the research work is to develop an appropriate technology for recovery of bioenergy from tannery solid waste.

The specific objectives of the research project are:

- To study the existing condition of tannery estate in the perspective of solid waste management.
- To assess the characteristics of tannery solid waste, domestic sewage for using as substrate in the biogas digesters.
- To setup some laboratory scale biogas units using tannery solid waste fleshings with cowdung and domestic sewage as substrate in different VS concentrations.
- To examine the performance of the biogas units set up by using amended tannery solid waste fleshings.
- To determine the optimum conditions for biogas generation from tannery solid waste fleshings.
- To study the economic feasibility of the technology.

1.4 Organization of the Thesis

The thesis comprises of six chapters. The first chapter is introduction providing an overall view of the study. Chapter two contains a brief and selective review of the relevant literature that provides general idea about anaerobic digestion. Description of the biochemical process, different parameters, chemical reactions, previous study related information, etc, all are gathered here. In chapter three overview of tannery industry is presented. It includes all the data related to solid waste management of tannery industry. In chapter four, methodologies took up for carrying out the research work are described. Chapter five examines the performance of biogas unit in terms of VS concentration, gas yield, pH control, biodegradation kinetics, etc. An economic analysis and the summary of the findingsare also describedin this chapter. Finally, in chapter six attempts are made to bring the major findings of the study together in the form of conclusions and outline the recommendations forthe studies to be required in future.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Anaerobic biomethane formation is a complex process, in which organic compounds are mineralized to biogas. It consists of several phases, such as hydrolysis, acidogenesis, acetogenesis and methanation, carried out by different groups of microorganisms, which partly stand in syntrophic interrelation and depend on different requirements in the environment (Deublein and Steinhauser, 2008). For instance, lipids are first hydrolyzed by acidogenic bacteria to glycerol and free long-chain fatty acids; furthermore glycerol is converted to acetate, while fatty acids convert to acetate, propionate and hydrogen. Finally, methanogenicbacteria which utilize methanol, acetate or hydrogen and carbon dioxide, produce methane (Cirne et al, 2007; Deublein and Steinhauser, 2008).

Among the many biological treatment methods experimented so far, anaerobic digestion possesses several advantages such as low energy requirement, low sludge production, low nutrient requirements and possibility of operation at high organic loading rate at a relatively low hydraulic retention time (Oliveira et al, 2004).

Disposal of waste generated in leather production is a serious problem and the importance of technological measures to combat environmental challenges from leather processing activities is now increasingly recognized.

2.2 Advantages of Biogas Technologies

The production and utilization of biogas from anaerobic digestion provides environmental and socioeconomic benefits for the society as a whole as well as for the involved farmers. Utilization the internal value chain of biogas production enhances local economic capabilities, safeguards jobs in rural areas and increases regional purchasing power. It improves living standards and contributes to economic and social development.

2.2.1 Benefits for the society

Renewable energy source

The current global energy supply is highly dependent on fossil sources (crude oil, lignite, hard coal, natural gas). These are fossilized remains of dead plants and animals, which have been exposed to heat and pressure in the Earth's crust over hundreds of millions of years. For this reason, fossil fuels are non-renewable resources which reserves are being depleted much faster than new ones are being formed.

The World's economies are dependent today of crude oil. There is some disagreement among scientists on how long this fossil resource will last but according to researchers, the "peak oil production"* has already occurred or it is expected to occur within the next period.

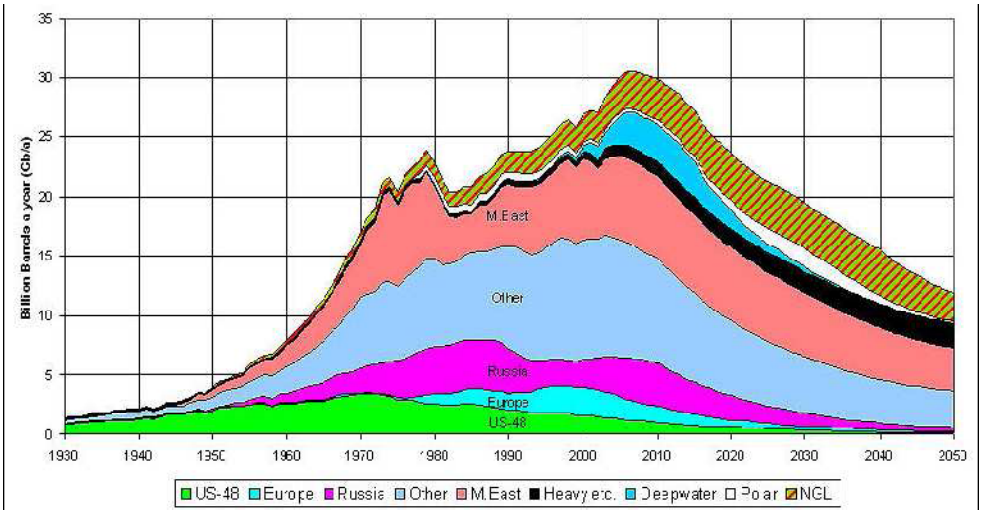

Figure 2.1: Scenario of World oil production and "peak oil" (ASPO 2008)

***The peak oil production is defined as "the point in time at which the maximum rate of global production of crude oil is reached, after which the rate of production enters its terminal decline"**

Unlike fossil fuels, biogas from anaerobic digestion is permanently renewable, as it is produced on biomass, which is actually a living storage of solar energy through photosynthesis. Biogas from Anaerobic digestion will not only improve the energy balance of a country but also make an important contribution to the preservation of the natural resources and to environmental protection.

Reduced greenhouse gas emissions and mitigation of global warming

Utilization of fossil fuels such as lignite, hard coal, crude oil and natural gas converts carbon, stored for millions of years in the Earth's crust, and releases it as carbon dioxide (CO_2) into the atmosphere. An increase of the current CO_2 concentration in the atmosphere causes global warming as carbon dioxide is a greenhouse gas (GHG). The combustion of biogas also releases CO_2. However, the main difference, when compared to fossil fuels, is that the carbon in biogas was recently up taken from the atmosphere, by photosynthetic activity of the plants. The carbon cycle of biogas is thus closed within a very short time (between one and several years). Biogas production by anaerobic digestion reduces also emissions of methane (CH_4) and nitrous oxide (N_2O) from storage and utilization of untreated animal manure as fertilizer. The GHG potential of methane is higher than of carbon dioxide by 23 fold and of nitrous oxide by 296 fold (Seadi et al, 2008). When biogas displaces fossil fuels from energy production and transport, a reduction of emissions of CO_2, CH_4 and N_2O will occur, contributing to mitigate global warming.

Reduced dependency on imported fossil fuels

Fossil fuels are limited resources, concentrated in few geographical areas of our planet. This creates, for the countries outside this area, a permanent and insecure status of dependency on import of energy. Most European countries are strongly dependent on fossil energy imports from regions rich in fossil fuel sources such as Russia and the Middle East (Seadi et al, 2008). Developing and implementing renewable energy systems such as biogas from anaerobic digestion, based on national and regional biomass resources, will increase security of national energy supply and diminish dependency on imported fuels.

Waste reduction

One of the main advantages of biogas production is the ability to transform waste material into a valuable resource, by using it as substrate for Anaerobic Digestion. Biogas production is an excellent way to utilize organic wastes for energy production, followed by recycling of the digested substrate as fertilizer.Anaerobic Digestion can also contribute to reducing the volume of waste and of costs for waste disposal (Seadi, 2001).

Job creation

Production of biogas from anaerobic digestion requires work power for production, collection and transport of anaerobic digestion feedstock, manufacture of technical equipment, construction, operation and maintenance of biogas plants. This means that the development of a national biogas sector contributes to the establishment of new enterprises, some with significant economic potential, increases the income in rural areas and creates new jobs.

Flexible and efficient end use of biogas

Biogas is a flexible energy carrier, suitable for many different applications. One of the simplest applications of biogas is the direct use for cooking and lighting, but in many countries biogas is used now-a-days for combined heat and power generation (CHP) or it is upgraded and fed into natural gas grids, used as vehicle fuel or in fuel cells.

Low water inputs

Even when compared to other biofuels, biogas has some advantages. One of them is that the anaerobic digestion process needs the lowest amount of process water. This is an important aspect related to the expected future water shortages in many regions of the world.

2.2.2 Benefits for the farmers

Digestate is an excellent fertilizer

A biogas plant is not only a supplier of energy. The digested substrate, usually named digestate, is a valuable soil fertilizer, rich in nitrogen, phosphorus, potassium and micronutrients, which can be applied on soils with the usual equipment for application of liquid manure. Compared to raw animal manure, digestate has improved fertilizer efficiency due to higher homogeneity and nutrient availability, better C/N ratio and significantly reduced odours (Seadi et al, 2008).

Table 2.1: Nutrient Values of organic matter

Manure	N,%	P_2O5, %	K_2O,%
Biogas Plant Residue	1.4-2.5	1.0	0.8
Farm yard Manure	0.5	0.2	0.5
Town Compost	1.5	1.0	1.5
Water Hyacinth	3.14	.85	3.45

Source: KVIC, 1975

Closed nutrient cycle

From the production of feedstock to the application of digestate as fertilizer, the biogas from anaerobic digestion provides a closed nutrient and carbon cycle. The methane (CH_4) is used for energy production and the carbon dioxide (CO_2) is released to the atmosphere and re-uptaken by vegetation during photosynthesis. Some carbon compounds remain in the digestate, improving the carbon content of soils, when digestateis applied as fertiliser.Biogas production can be perfectly integrated into conventional and organic farming, where digestate replaces chemical fertilizers, produced with consumption of large amounts of fossil energy.

Flexibility to use different feedstock

Various types of feedstock can be used for the production of biogas: animal manure and slurries, crop residues, organic wastes from dairy production, food industries and agro industries, wastewater sludge, organic fraction of municipal solid wastes, organic wastes from households and from catering business as well as energy crops. Biogas can also be collected, with special installations, from landfill sites.

One main advantage of biogas production is the ability to use “wet biomass” types as feedstock, all characterized by moisture content higher than 60–70% (e.g. sewage sludge, animal slurries, flotation sludge from food processing etc.). In recent years, a number of energy crops (grains, maize, rapeseed), have been largely used as feedstock for biogas production in countries like Austria or Germany (Seadi et al, 2008). Besides energy crops, all kinds of agricultural residues, damaged crops, unsuitable for food or resulting from unfavorable growing and weather conditions, can be used to produce biogas and fertilizer. A number of animal by-products, not suitable for human consumption, can also be processed in biogas plants.

Reducesodours and flies

Storage and application of liquid manure, animal dung and many organic wastes are sources of persistent, unpleasant odours and attract flies. Anaerobic Digestion reduces these odours by up to 80% (Seadi and Nielsen, 2004). Digestate is almost odorless and the remaining ammonia odours disappear shortly after application as fertilizer.

Veterinary safety

Application of digestate as fertilizer, compared to application of untreated manure and slurries, improves veterinary safety. In order to be suitable for use as fertilizer, digestateis submitted to a controlled sanitation process. Depending of the type of feedstock involved, sanitation can be provided by theanaerobic digestion process itself (Seadi et al, 2008), through a minimum guaranteed retention time of the substrate inside the digester, at thermophilic temperature, or it can be done in a separate process step, by pasteurization or by pressure sterilization. In all cases, the aim of sanitation is to inactivate pathogens, weed seeds and other biological hazards and to prevent disease transmission through digestate application.

2.3 The Mechanism of Anaerobic Digestion

Anaerobic digestion is a multi-stage process occurring in the absence of oxygen, where bacteria are the primary organisms involved (Bingemer and Crutzen). Anaerobic digestion converts waste organic materials to produce: mostly methane (CH_4) and carbon dioxide (CO_2) and very small amounts of other gasses such as hydrogen sulphide (H_2S), ammonia (NH_3), depending on the composition of feed materials. In a biogas installation, the result of the anaerobic digestion process is the biogas and the digestate. If the substrate for anaerobic digestion is a homogenous mixture of two or more feedstock types (e.g. animal slurries and organic wastes from food industries), the process is called “co–digestion” and is common to most biogas applications today (Moller et al, 2004).

2.4 Substrates for Anaerobic Digestion

A wide range of biomass types can be used as substrates (feedstock) for the production of biogas from anaerobic digestion.

Table2.2: Effect of additives on gas production with cowdung

Additives	**Gas Production**			
	Gas(m^3/kg)	Methane (%)	H_2 (%)	CO_2 (%)
Nill	.063	60	1.1	34.4
Leguminous leaves,2.4%	.063	61.6	4.0	32.0
Non Leguminous leaves,20%	.081	68.0	.6	28
Sarson oil cake,1.2%	0.063	67.7	-	30.4
Cellulose,1%	.084	52.8	-	44.0
Ashes,1%	.061	60.4	2.9	34.4
Casein,0.4%	.087	64.0	2.4	32.0
Cane sugar,0.4%	.070	57.6	2.1	38.4
Cane Sugar,1%+urea,1%	.087	68.0	-	30.6
Cane sugar,1%+CaCO3,1%	.091	70.0	-	28.0
Charcoal,4%	.065	65.6	-	32.0
Non Leguminous leaves,20%	.081	68.0	.6	28
Sarson oil cake,1.2%	0.063	67.7	-	30.4
Cellulose,1%	.084	52.8	-	44.0
Ashes,1%	.061	60.4	2.9	34.4
Casein,0.4%	.087	64.0	2.4	32.0
Cane sugar,0.4%	.070	57.6	2.1	38.4
Cane Sugar,1%+urea,1%	.087	68.0	-	30.6
Cane sugar,1%+CaCO3,1%	.091	70.0	-	28.0
Charcoal,4%	.065	65.6	-	32.0

Source : KVIC, 1975

2.5 The Biochemical Process of Anaerobic Digestion

As previously stated, anaerobic digestion is a microbiological process of decomposition of organic matter in absence of oxygen. The main products of this process are biogas and digestate consisting primarily of methane and carbon dioxide. Digestate is the decomposed substrate, resulted from the production of biogas.

During anaerobic digestion, very little heat is generated in contrast to aerobic decomposition (in presence of oxygen), like it is the case of composting. The energy, which is chemically bounded in the substrate, remains mainly in the produced biogas, in form of methane.

The process of biogas formation is a result of linked process steps, in which the initial material is continuously broken down into smaller units. Specific groups of micro-organisms are involved in each individual step. These organisms successively decompose the products of the previous steps.

The simplified diagram of the anaerobic digestion process, shown in Figure 2.2, highlights the four main process steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis.

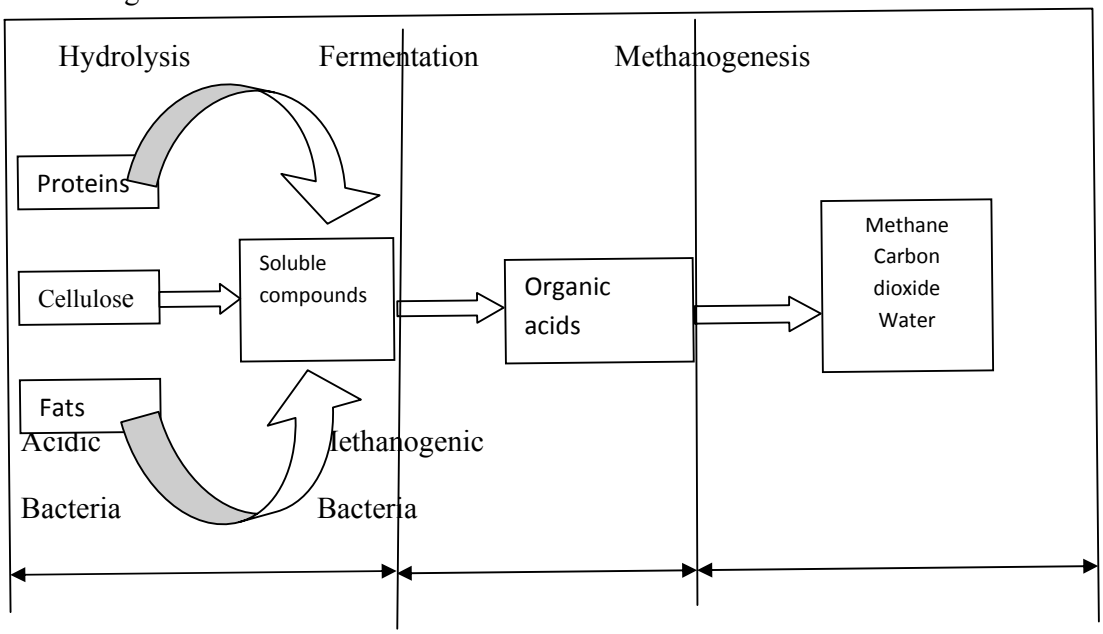

Figure 2.2: Different stages of anaerobic digestion (courtesy: US dept of Energy)

The process steps quoted in Figure 2.2 run parallel in time and space, in the digester tank. The speed of the total decomposition process is determined by the slowest

reaction of the chain. In the case of biogas plants, processing vegetable substrates containing cellulose, hemi-cellulose and lignin, hydrolysis is the speed determining process. During hydrolysis, relatively small amounts of biogas are produced. Biogas production reaches its peak during methanogenesis.

2.5.1 Hydrolysis

Hydrolysis is theoretically the first step of anaerobic digestion, during which the complex organic matter (polymers) is decomposed into smaller units (mono- and oligomers). During hydrolysis, polymers like carbohydrates, lipids, nucleic acids and proteins are converted into glucose, glycerol, purines and pyridines. Hydrolytic microorganisms excrete hydrolytic enzymes, converting biopolymers into simpler and soluble compounds as it is shown below:

Lipids —— *lipase* ⟶ *fatty acids, glycerol*

Polysaccharide ——— *cellulase, cellobiase, xylanase, amylase* ⟶ *monosaccharide*

Proteins —— *protease* ⟶ *amino acids*

A variety of microorganisms is involved in hydrolysis, which is carried out by exoenzymes, produced by those microorganisms which decompose the undissolved particulate material. It is a rate limiting step for waste containing higher percentage of lipids and other slow – hydrolyzing compounds (Kennedy and Van den Berg, 1982).The products resulted from hydrolysis are further decomposed by the microorganisms involved and used for their own metabolic processes.

2.5.2 Fermentation

Fermentation (acidogenesis and acetogenesis) soluble monomers are fermented to simple organic compounds, volatile fatty (acetic, butyric, prop ionic, and also lactic, formic) acids and in some situations, CO_2 and or hydrogen by acid-forming bacteria, depending on the composition of waste materials.

2.5.3 Acidogenesis

During acidogenesis, the products of hydrolysis are converted by acidogenic (fermentative) bacteria into methanogenic substrates. Simple sugars, amino acids and fatty acids are degraded into acetate, carbon dioxide and hydrogen (70%) as well as into volatile fatty acids (VFA) and alcohols (30%) (Seadi et al, 2008).

2.5.4 Acetogenesis

Products from acidogenesis, which cannot be directly converted to methane by methanogenic bacteria, are converted into methanogenic substrates during acetogenesis. VFA and alcohols are oxidized into methanogenic substrates like acetate, hydrogen and carbon dioxide. VFA, with carbon chains longer than two units and alcohols, with carbon chains longer than one unit, are oxidized into acetate and hydrogen. The production of hydrogen increases the hydrogen partial pressure. This can be regarded as a waste productof acetogenesis and inhibits the metabolism of the acetogenic bacteria. During methanogenesis, hydrogen is converted into methane. Acetogenesis and methanogenesis usually run parallel, as symbiosis of two groups of organisms.

2.5.5 Methanogenesis

Methanogenesis methane is produced from methanogenic substrates or from the reduction of carbon dioxide by hydrogen using acetotrophic and hydrogenotrophic bacteria respectively (Rahman and Muyeed, 2010). The hydrogen consumption also improves the environment of the conversion process of butyrate and propionate to acetone. Methanogenic substrates generally include acetate, methanol, format, methylamines, methyl mercaptants and reduced metals (Palmisano and Barlaz, 1996). Micro-organisms may also directly produce methane from carbon monoxide, carbon dioxide and hydrogen.

Acetic acid ⟶ methanogenic bacteria ⟶ *methane + carbon dioxide*

Hydrogen + carbon dioxide ⟶ methanogenic bacteria ⟶ *methane + water*

Methanogenesis is a critical step in the entire anaerobic digestion process, as it is the slowest biochemical reaction of the process (Seadi et al, 2008). Methanogenesisis severely influenced by operation conditions. Composition of feedstock, feeding rate, temperature, and pH are examples of factors influencing the methanogenesis process. Digester overloading, temperature changes or large entry of oxygen can result in termination of methane production.

2.6 Chemical Reactions

All the above process is successive, but in a continuous-feed digester they may take place at any time. The better the different fermentation process merge the shorter the digestion period. The general anaerobic transformation of solid waste described by Rahman and Muyeed (2010) by means of the following equations:

Organic matter + H_2O + nutrients ⟶ new cell + Resistant organic matter +CO_2+CH_4 +NH_4 + H_2S + Heat

For practical purposes, the overall conversion of the organic fraction of solid waste to methane, carbon dioxide and ammonia can be represented with the following equations:

$C_aH_bO_cN_dn \longrightarrow C_WH_XO_yN_z + m\ CH_4 + sCO_2 + r\ H_2O + (d-nx)\ NH_3$

Where,

$s = a-nw-m$

$r = c-ny-2s$

The term$C_aH_bO_cN_d$ and $nC_WH_XO_yN_z$ are used to represent (on a molar basis) the composition of the organic material present at the start and the end of the process respectively. If it is assumed that the organic wastes are established completely, the corresponding expression is

$$C_aH_bO_cN_d + \frac{4a-b-2c+3d}{4} H_2O \longrightarrow \left(\frac{4a+b-2c-3d}{8}\right) CH_4 + \left(\frac{4a-b+2c+3d}{8}\right) CO_2 + dNH_3$$

In operation where solid wastes have been mixed with wastewater sludge, it has been found that the gas collected from the digester contains between 50 and 60 percent methane. It has also been found that about 10 to 16 ft^3 of gas is produced per pound of biodegradable volatile solids utilized.

The typical reaction that takes place in hydrolysis process is:

$C_6H_{10}O_5 + 2H_2O \longrightarrow C_6H_{12}O_6$

The typical reaction that may take place in the fermentation process caused by acid – forming bacteria are:

$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH$ (acetate) + $2CO_2 + 4H_2$

$C_6H_{12}O_6 \longrightarrow CH_3CH_2CH_2COOH$ (butyrate) + $2CO_2 + 2H_2$

$C_6H_{12}O_6 \longrightarrow CH_3CH_2COOH$ (propionate) + $2H_2O$

The butyrate and propionate cannot be utilized directly by methane producing bacteria. The acetogenic bacteria convert (Vigneswaran et al, 1986) them into acetate according to the reactions:

$CH_3CH_2CH_2COOH$ (butyrate) + $2H_2O \longrightarrow CH_3COOH$ (butyrate) + $2H_2$

CH_3CH_2COOH (propionate) + $2H_2O \longrightarrow CH_3COOH$ (acetate) + $CO_2 + 3H_2$

The typical reactions that may take place in the methanogenesis phase are:

CH_3COOH (acetate) $\longrightarrow CH_4 + CO_2$

$4H_2 + H^+ + HCO_3^-$ (hydrogen and carbon dioxide) $\longrightarrow 3CH + 3H_2O$

$4CH_3OH$ (methanol) $\longrightarrow 3CH_4 + CO_2 + 3H_2O$

$4HCOOH$ (format) $\longrightarrow CH_4 + 3\ CO_2 + 2H_2O$

$4(CH_3)\ NH_2$ (monomethylamin) $+H_2O \longrightarrow 3CH_4 + CO_2 + 4NH_3$

$2(CH_3)_2NH$ (dimethylamin) $+2H_2O \longrightarrow 3CH_4 + 2CO_2 + 2NH_3$

$4(CH_3)_3NH_2$ (trimethylamin) $+6H_2O \longrightarrow 9CH_4 + 3CO_2 + 4NH_3$

$2(CH_3)\ S$ (methyl mercaptants) $+3H_2O \longrightarrow 3CH_4 + CO_2 + H_2S$

$4M^0$ (metals) $+8H^+ + CO_2 \longrightarrow 4M^{++} + CH_4 + 2H_2O$

2.7 Anaerobic Digestion Parameters

The efficiency of anaerobic digestion is influenced by some critical parameters, thus it is crucial that appropriate conditions for anaerobic microorganisms are provided. The growth and activity of anaerobic microorganisms is significantly influenced by conditions such as exclusion of oxygen, constant temperature, and pH-value, nutrient supply, stirring intensity as well as presence and amount of inhibitors (e.g. ammonia). The methane bacteria are fastidious anaerobes, so that the presence of oxygen into the digestion process must be strictly avoided.

2.7.1 Temperature

The anaerobic digestion process can take place at different temperatures, divided into three temperature ranges: psychrophilic (below 25°C), mesophilic (25°C – 45°C), and thermophilic (45°C –70°C). There is a direct relation between the process temperature and the HRT (Table 2.3).

Table 2.3: Thermal stage and typical retention times

Thermal stage	Process temperatures	Minimum retention time
Psychrophilic	< 20 °C	70 to 80 days
Mesophilic	30 to 42 °C	30 to 40 days
Thermophilic	43 to 55 °C	15 to 20 days

Source: Seadi et al, 2008

The temperature stability is decisive forAnaerobic Digestion. In practice, the operation temperature is chosen with consideration to the feedstock used and the necessary process temperature is usually provided by floor or wall heating systems, inside the digester. Figure 2.3 shows the rates of relative biogas yields depending on temperature and retention time.

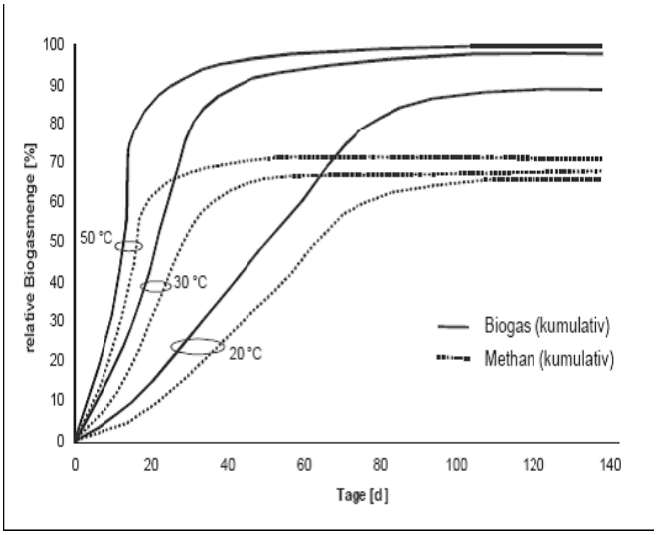

Figure 2.3: Relative biogas yields, depending on temperature and retention time (LfU, 2007)

Many modern biogas plants operate at thermophilic process temperatures as the thermophilic process provides many advantages, compared to mesophilic and psychrophilic processes:

- effective destruction of pathogens
- higher growth rate of methanogenic bacteria at higher temperature
- reduced retention time, making the process faster and more efficient
- improved digestibility and availability of substrates
- better degradation of solid substrates and better substrate utilization
- better possibility for separating liquid and solid fractions

The thermophilic process has also some disadvantages:

- larger degree of imbalance
- larger energy demand due to high temperature
- higher risk of ammonia inhibition

Operation temperature influences the toxicity of ammonia. Ammonia toxicity increases with increasing temperature and can be relieved by decreasing the process temperature. However, when decreasing the temperature to 50°C or below, the growth rate of the thermophilic microorganisms will drop drastically, and a risk of washout of the microbial population can occur, due to a growth rate lower than the actual HRT (Angelidaki, 2004). This means that a well functioningthermophilic digester can be loaded to a higher degree or operated at a lower HRT than an e.g. mesophilic one because of the growth rates of thermophilic organisms (Figure 2.4). Experience shows that at high loading or at low HRT, a thermophilic operated digester has higher gas yield and higher conversion rates than a mesophilic digester.

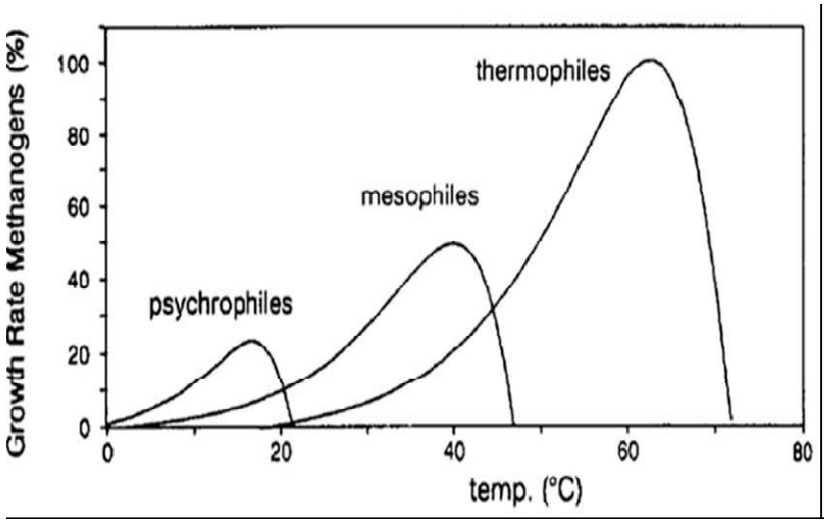

Figure 2.4: Relative growth rates of methanogens (Angelidaki, 2004)

The solubility of various compounds (NH_3, H_2, CH_4, H_2S and VFA) also depends on the temperature. This can be of great significance for materials which have an inhibiting effect on the process.

The viscosity of theanaerobic digestion substrate is inversely proportional to temperature. This means that the substrate is more liquid at high temperatures and the diffusion of dissolved material is thus facilitated. Thermophilic operation temperature results in faster chemical reaction rates, thus better efficiency of methane production, higher solubility and lower viscosity.

The higher demand for energy in the thermophilic process is justified by the higher biogas yield. It is important to keep a constant temperature during the digestion process, as temperature changes or fluctuations will affect the biogas production negatively. Thermophilic bacteria are more sensitive to temperature fluctuation of ±1°C and require longer time to adapt to a new temperature, in order to reach the maximum methane production. Mesophilic bacteria are less sensitive. Temperature fluctuations of ± 3°C are tolerated, without significant reductions in methane production.

2.7.2 pH-values and optimum intervals

The pH-value is the measure of acidity/alkalinity of a solution (respectively of substrate mixture, in the case of anaerobic digestion) and is expressed in *parts per million* (ppm) (Barrow, 1979). The pH value of the anaerobic digestion substrate influences the growth of methanogenic microorganisms and affects the dissociation of some compounds of importance for the anaerobic digestion process (ammonia, sulphide, organic acids). Experience shows that methane formation takes place within a relatively narrow pH interval, from about 5.5 to 8.5, with an optimum interval between 7.0-8.0 for most methanogens. Acidogenic microorganisms usually have lower value of optimum pH.

The optimum pH interval for mesophilic digestion is between 6.5 and 8.0 and the process is severely inhibited if the pH-value decreases below 6.0 or rises above 8.3(Seadi et al, 2008). The solubility of carbon dioxide in water decreases at increasing temperature. The pH-value in thermophilic digesters is therefore higher than in mesophilic ones, as dissolved carbon dioxide forms carbonic acid by reaction with water.

The value of pH in anaerobic reactors is mainly controlled by the bicarbonate buffer system. Therefore, the pH value inside digesters depends on the partial pressure of CO_2 and on the concentration of alkaline and acid components in the liquid phase. If accumulation of base or acid occurs, the buffer capacity counteracts these changes in pH, up to a certain level. When the buffer capacity of the system is exceeded, drastic changes in pH-values occur, completely inhibiting the anaerobic digestion process. For this reason, the pH-value is not recommended as a stand-alone process monitoring parameter.

The buffer capacity of theanaerobic digestion substrate can vary. Experience from Denmark shows that the buffer capacity of cattle manure varies with the season, possibly influenced by the composition of the cattle feed. The pH-value of domestic animal manure is therefore a variable which is difficult to use for identification of process imbalance, as it changes very little and very slowly. It is, however, important to note that the pH-value can be quick, relatively reliable and cheap way of registering system imbalance in more weakly buffered systems, such as anaerobic digestion of various wastewater types.

The experimental result, carried out at Chengdu Research Institute, China, with varying the pH of input materials, shows a maximum output of biogas at pH from 7.5 to 8.0.

Table2.4: Effect of pH on yield of biogas

Starting pH	5	5	7	8	9	10
Final pH	6	7	7	7.5	7	7
Total output of biogas(m^3)	12.70	14.80	22.50	24.69	19.89	10.25

Source: Rahman and Muyeed, 2010

2.7.3 Volatile fatty acids (VFA)

The stability of theanaerobic digestion process is reflected by the concentration of intermediate products like the VFA. The VFA are intermediate compounds (acetate, propionate, butyrate, lactate), produced during acidogenesis, with a carbon chain of up to six atoms. In most cases,anaerobic digestion process instability will lead to accumulation of VFA inside the digester, which can lead furthermore to a drop of pH-value. However, the accumulation of VFA will not always be expressed by a drop of pH value, due to the buffer capacity of the digester, through the biomass types contained in it.

Practical experience shows that two different digesters can behave totally different in respect to the same VFA concentration, so that one and the same concentration of VFA can be optimal for one digester, but inhibitory for the other one. One of the possible explanations can be the fact that the composition of microorganism populations varies from digester to digester. For this reason, and like in the case of pH, the VFA concentration cannot be recommended as a stand-alone process monitoring parameter.

2.7.4 Ammonia

Ammonia (NH_3) is an important compound, with a significant function for the anaerobic digestion process. NH_3 is an important nutrient, serving as a precursor to foodstuffs and fertilizers and is normally encountered as a gas, with the characteristic pungent smell. Proteins are the main source of ammonia for the anaerobic digestion process (Wikipedia).

Too high ammonia concentration inside the digester, especially free ammonia (the unionized form of ammonia), is considered to be responsible for process inhibition. This is common to anaerobic digestion of animal slurries, due to their high ammonia concentration, originating from urine. For its inhibitory effect, ammonia concentration should be kept below 80 mg/l. Methanogenic bacteria are especially sensitive to ammonia inhibition. The concentration of free ammonia is direct proportional to temperature, so there is an increased risk of ammonia inhibition of anaerobic digestion processes operated at thermophilic temperatures, compared to mesophilic ones. The free ammonia concentration is calculated from the equation:

$$[NH_3] = \frac{[T\text{-}NH_3]}{(1 + \frac{H^+}{ka})}$$

Where *[NH3]* and *[T-NH3]* are the free and respectively the total ammonia concentrations, and *ka*is the dissociation parameter, with values increasing with temperature. This means that increasing pH and increasing temperature will lead to increased inhibition, as these factors will increase the fraction of free ammonia. When a process is inhibited by ammonia, an increase in the concentration of VFA will lead to a decrease in pH. This will partly counteract the effect of ammonia due to a decrease in the free ammonia concentration(Seadi et al 2008).

2.7.5 Macroand micronutrients (trace elements) and toxic compounds

Microelements (trace elements) like iron, nickel, cobalt, selenium, molybdenum or tungsten are equally important for the growth and survival of the anaerobic digestion microorganisms as the macronutrients carbon, nitrogen, phosphor, and sulphur. The optimal ratio of the macronutrients carbon, nitrogen, phosphor, and sulphur (C: N: P: S) is considered 600:15:5:1. Insufficient provision of nutrients and trace elements, as

well as too high digestibility of the substrate can cause inhibition and disturbances in theanaerobic digestion process.

Another factor, influencing the activity of anaerobic microorganisms, is the presence of toxic compounds. They can be brought into the anaerobic digestion system together with the feedstock or are generated during the process.

2.8 Operational Parameters

2.8.1 Organic load

The construction and operation of a biogas plant is a combination of economical and technical considerations. Obtaining the maximum biogas yield, by complete digestion of the substrate, would require a long retention time of the substrate inside the digester and a correspondingly large digester size. In practice, the choice of system design (digester size and type) or of applicable retention time is always based on a compromise between getting the highest possible biogas yield and having justifiable plant economy. In this respect, the organic load is an important operational parameter, which indicates how much organic dry matter can be fed into the digester, per volume and time unit, according to the equation below:

$B_R = m * c / V_R$

$B_R$organic load [kg/d*m³]

mmass of substrate fed per time unit [kg/d]

cconcentration of organic matter [%]

$V_R$digester volume [m³]

2.8.2 Hydraulic retention time (HRT)

An important parameter for dimensioning the biogas digester is the hydraulic retention time (HRT). The HRT is the average time interval when the substrate is kept inside the digester tank. HRT is correlated to the digester volume and the volume of substrate fed per time unit, according to the following equation

$HRT = V_R/V$

HRT hydraulic retention time [days]

$V_R$digester volume [m³]

V volume of substrate fed per time unit [m³/d]

According to the above equation, increasing the organic load reduces the HRT. The retention time must be sufficiently long to ensure that the amount of microorganisms removed with the effluent (digestate) is nothigher than the amount of reproduced microorganisms. The duplication rate of anaerobic bacteria is usually 10 days or more (Metcalf and Eddy, 1979). A short HRT provides a good substrate flow rate, but a lower gas yield. It is therefore important to adapt the HRT to the specific decomposition rate of the used substrates. Knowing the targeted HRT, the daily feedstock input and the decomposition rate of the substrate,it is possible to calculate the necessary digester volume.

2.8.3 Nutrients

The growth and catabolism of microbes need various kinds of nutrients, especially elements of carbon, nitrogen and phosphorus are necessary. Hence, besides the property of gas production of feedstock, it is also necessary to take the proper ratio of carbon and nitrogen (C/N) into account. Carbon is utilized for energy and nitrogen for the building of the cell structure. A specific group of microbes always consume these two elements in proportion. So far there are still various views existing on the proper C: N ratio of feedstock in rural areas. Some people hold that the ratio may not be so strict in biogas fermentation, but it is commonly recognized that a C/N ratio of 20-30: 1 is acceptable.

It is useful to prepare feedstock at a certain proportion of carbon and nitrogen in biogas fermentation. In fact, the raw materials for biogas fermentation are very complex, and carbon and nitrogen in organic materials exist in different ways. Both lignin and glucose are carbon compounds. Glucose is easy to be degraded by microbes to produce methane whereas lignin is very difficult (Schonborn, 1986). Different nitrogen – compounds have different capabilities in degradation and utilization by microbes. Thus, for C/N ratio of feedstock it is necessary to draw a line of demarcation between those raw materials in which carbon or nitrogen is easy to be utilized and those in which carbon or nitrogen is difficult to be utilized. Based on the content of carbons and nitrogen in the feedstock we can calculate the C/N ratio using the following formula.

$$K = \frac{C_1X_1 + C_2X_2 + ... + C_nX_n}{N_1X_1 + N_2X_2 + ... + N_nX_n} = \frac{\sum C_iX_i}{\sum N_iX_i}$$

Where

C = Percentage of carbon in the raw material

N = Percentage of nitrogen in the raw material

X = weight of the raw material

K = C/N ratio of mixed raw material

The table 2.5 shows the percentages of nitrogen content and the values of C/N ratio of some selected waste products.

Table 2.5: Nitrogen and C/N ratios of selected waste products

	Nitrogen,% of dry weight	C/N ratio
Dry wheat straws[1]	0.53	87
Dry rice straws[1]	0.53	67
Corn stalks[1]	0.75	53
Fallen leaves[1]	1	41
Wild grass[1]	0-54	27
Weeds[2]	2	19
Food waste	1.5-2.8	15-25
Paper[2]	0.2	170
Urine[2]	15-18	0.8
Fresh human waste[1]	0.85	2.9
Fresh cattle dung	0.29	25
Buffalo dung	1.5-1.7	18-20
Fresh pig manure[1]	3.78	13
Fresh sheepdroppings[1]	3.78	30
Poultry manure	6.31	5

Source: APH (1989)[1], Oben and Wright (1987)[2]

2.8.4 Mixing

Many substrates and various modes of fermentation require some sort of substrate mixing or mixing in order to maintain process stability within the digester. The most important objectives of mixing are:

- removal of the metabolites produced by the methanogens (gas)
- mixing of fresh substrate and bacterial population (inoculation)
- preclusion of scum formation and sedimentation

- avoidance of pronounced temperature gradients within the digester
- provision of a uniform bacterial population density
- prevention of the formation of dead spaces that would reduce the effective digester volume.

Mixing of the digester contents is important for the trouble-free performance of a biogas-plant. For the following reasons mixing is recommended several times a day:

- to avoid and destroy swimming and sinking layers
- to improve the activity of bacteria through release of biogas and provision of fresh nutrients
- to mix fresh and fermenting substrate in order to inoculate the former
- to arrive at an even distribution of temperature thus providing uniform conditions inside the digester

A well agitated substrate can, leaving other parameters constant, increase its biogas production by 50%.

In selecting or designing a suitable means of mixing, the following points should be considered:

1. The process involves a symbiotic relationship between various strains of bacteria, i.e. the metabolite from one species can serve as nutrient for the next species, etc. Whenever the bacterial community is disrupted, the process of fermentation will remain more or less unproductive until an equivalent new community is formed. Consequently, excessive or too frequent mixing is usually detrimental to the process. Slow stirring is better than rapid mixing.
2. A thin layer of scum must not necessarily have an adverse effect on the process. For systems in which the digester is completely filled with substrate, so that any scum always remains sufficiently wet, there is little or no danger that the extraction of gas could be impeded by the scum.
3. Some types of biogas systems can function well without any mechanical mixing at all. Such systems are usually operated either on substrates with such a high solid content, that no stratification occurs, or on substrates consisting primarily of solute substances.

Mixing, as a general rule, should be performed as much as necessary but as little as possible. Too frequent mixing with fast rotating; mechanical mixing devices can

disturb the biological processes in the biological processes in the fermenting substrate. In addition, an all-too thorough mixing of the whole digester contents may lead to half-digested substrate leaving the digester prematurely. Hydrolysis turns polymer to monomer. In many cases hydrolysis is a slow process but because of mixing in the inlet tank the mixer become homogenous and expedite the biomethanation process. Sometimes addition of enzyme is necessary for biomethanation process (Rouf et al, 2010).

2.9 Digesters

The core of a biogas plant is the digester - an air proof reactor tank, where the decomposition of feedstock takes place, in absence of oxygen, and where biogas is produced. Common characteristics of all digesters, apart from being air proof, are that they have a system of feedstock feed-in as well as systems of biogas and digestate output. In European climates anaerobic digesters have to be insulated and heated.

There are a various types of biogas digesters, operating in Europe and around the world. Digesters can be made of concrete, steel, brick or plastic, shaped like silos, troughs, basins or ponds, and they may be placed underground or on the surface. The size of digesters determine the scale of biogas plants and varies from few cubic meters in the case of small household installations to several thousands of cubic meters, like in the case of large commercial plants, often with several digesters.

The design of a biogas plant and the type of digestion are determined by the dry matter content of the digested substrate. As mentioned before, anaerobic digestion operates with two basic digestion systems: wet digestion, when the average dry matter content of the substrate is lower than 15 % and dry digestion, when the dry matter content of the substrate is above this value, usually between 20-40 %. These definitions and their limit values have some regional variations or they can be differentiated by legislation and support schemes, like e.g. in Germany.

Wet digestion involves feedstock like manure and sewage sludge, while dry digestion is applied to biogas production from solid animal manure, with high straw content, household waste and solid municipal biowaste, green cuttings and grass from landscape maintenance or energy crops (fresh or ensiled) (Seadi et al, 2008).

From the point of view of feedstock input and output, there are two basic digester types: batch and continuous.

2.9.1 Batch-type digesters

The specific operation of batch digesters is that they are loaded with a portion (batch) of fresh feedstock, which is allowed to digest and then is completely removed. The digester is fed with a new portion and the process is repeated. Batch-type digesters are the simplest to build and are usually used for dry digestion.

An example of batch digesters are the so-called “garage type” digesters made of concrete, for the treatment of source separatedbiowaste from households, grass cuttings, solid manure and energy crops. Treatment capacity ranges from 2000 to 50000 tons per year. The feedstock is inoculated with digestate and fed in the digester. Continuous inoculation with bacterial biomass occurs through recirculation of percolation liquid, which is sprayed over the substrate in the digester.

Unlike wet digestion, dry digestion needs no stirring or mixing of the anaerobic digestion substrate during digestion. The temperature of the process and of percolation liquid are regulated by a built-in floor heating system, inside the digester, and by a heat exchanger, which acts as a reservoir for percolation liquid. Compared to other systems, batch digestion has the advantage of low operation costs and costs of the mechanical technology behind it and the disadvantage of high process energy consumption and maintenance costs.

A promising alternative for complete dry digestion is the use of plastic bags or foil tubes. The idea is to reduce investment costs by using plastic sheeting from silo bag technology, where anaerobic digestion substrates (manure, biowastes) are stored in airtight plastic bags.

Batch digesters are also used for combined dry and wet digestion, in case of stackable feedstock types, where additional waste water or percolation liquid is used in larger quantities for flooding or percolation. The possibility to handle substrates, not only through pre-treatment and percolation, but also by high pressure “aeration” and flooding, enables dry fermentation to be used as a suitable treatment process for controlled landfills.

2.9.2 Continuous-type digesters

In a continuous-type digester, feedstock is constantly fed into the digester. The material moves through the digester either mechanically or by the pressure of the newly feed substrate, pushing out the digested material. Unlike batch-type digesters, continuous digesters produce biogas without interruption for loading new feedstock and unloading the digested effluent. Biogas production is constant and predictable.

Continuous digesters can be vertical, horizontal or multiple tank systems. Depending on the solution chosen for stirring the substrate, continuous digesters can be completely mixed digesters and plug flow digesters (Table 2.6). Completely mixed digesters are typically vertical digesters while plug-flow digesters are horizontal.

Table 2.6: Digester types

Completely mixed digesters	**plug flow digesters**
Round, simple tank construction, vertical	Elongated, horizontal tank
Completely mixed	vertically mixed
Suitable for simple feedstock (liquid manure)	Suitable for difficult feedstock (solid manure)
Fractions of the undigested feedstock can reach the outflow	Normally, no short cut between inflow and Outflow; secure sanitation
Process temperature 20° - 37° C	Process temperature 35° - 55° C
Retention time 30 - 90 days	Retention time 15 - 30 days

Source: Seadi et al, 2008

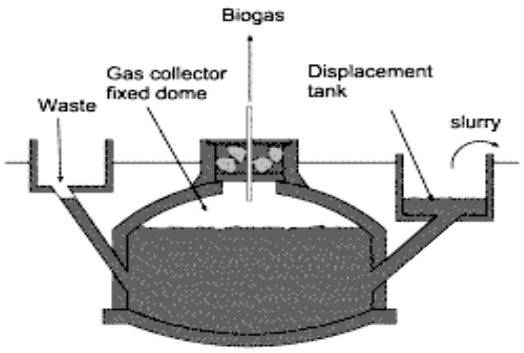

Figure 2.5: Chinese fixed dome plant plant**CAMARTEC design**

Source: TBW, Germany, 2001

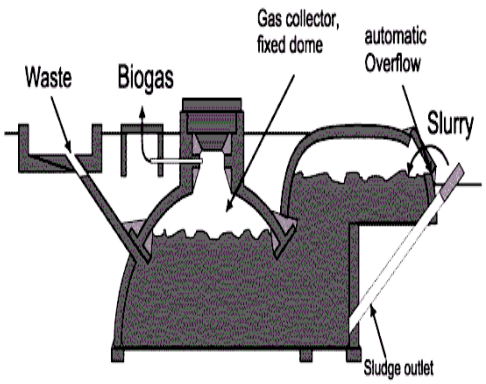

Figure 2.6: Fixed dome

2.10 Kinetics of Biogas Generation

Many attempts have been made by different investigators to formulate an expression to describethekineticsofanaerobic digestion (Rao and Singh, 2004, Vavilin et al, 2008). Many of these expressions are based on the study conducted by Mond (1950).According to Mond (1950), the microbial growth rate (dX/dt) is proportional to the rate of substrate (dS/dt) utilization as follows:

$(dX/dt) = Y (-dS/dt) = (XS\mu_{max})/ (K_s + S)$

Where,

X=micro- organism concentration (mg/l)

S=substrate concentration (mg COD /l)

Y= growth yield coefficient mg biomass per mg substrate

μ_{max} = maximum specific growth (/d)

K_S=half saturation constant (mg COD /l)

Although a number of expressions are available to describe the kinetics of anaerobic digestion, at the present stage of development of the kinetic theory of anaerobic digestion these have limited application as rational tools in the selection and design processes of this system (Van Haandel and Lattinga, 1994).

2.11 Biogas Technology in Leading Asian Countries

The international seminar on biogas technology held in Beijing, China, in October 2005 strongly illustrated the renewed interest shown in the application of anaerobic digestion in Asia and the Pacific region. Already, plans exist to spread biogas programmes throughout Asia.

According to the Chinese Ministry of Agriculture, 15 million households in rural China were using biogas by the end of 2004. The Ministry aims to increase this number to 27 million by 2010, which will account for over ten percent of all rural households. By the end of 2005 there were 2,492 medium and large-scale biogas digesters in livestock and poultry farms, while 137,000 biogas tanks had been constructed for the purification of household wastewater. In Sichuan Province alone 2.58 million domestic biogas plants had been constructed by the end of 2004. This number will increase to five million by the end of 2010.

In order to promote this growth, the new Renewable Energy Law of the People's Republic ofChina came into force on 1 January 2006, following its approval in 2005. This law establishes five systems to support the development of renewable energy resources market fostering andprotection, resource exploitation and planning, technical and industrial support, price support and cost sharing; and financial support and economic stimulation.

In India, the Ministry of Non-Conventional Energy Sources (MNES) continues to implement the National Biogas and Manure Management Programme (NBMMP) through State nodal departments and agencies, the Khadi and Village Industries Commission (KVIC) and a number of NGOs.

As many as 17,803 domestic biogas plants were installed from 2004 to 2005, bringing the total number installed under Nepal's Biogas Support Programme (BSP) since 1992 to over 140,000 farmers to purchase biogas systems.

(*www.unapcaem.org/publication/F-Biogas.PDF)*

2.12 Biogas Technology in Bangladesh

The institute for fuel research and development (IFRD) of the Bangladesh Council of Scientific and Industrial Research (BCSIR) has been the main actor for the dissemination of domestic biogas plant in Bangladesh until now. In total, close to 39,000 family sized biogas plant of different designs have been installed throughout Bangladesh so far. Table 2.7 shows the different organizations involved in the dissemination of biogas plants in Bangladesh and the number of plants installed: number of plants installed:

Table 2.7: Biogas plants constructed by different organizations in Bangladesh

Sl.	Organization	Period	Number of plants
1	BCSIR	1937-2005	22,100
2	LGED	1985-2001	7,000
3	DoE	1979-1983	260
4	BRAC	1987-2005	300
5	DLS	1988-1994	70
6	ThengamaraMohilaSabujSangha(TMSS)		
7	BSCIC	1983-1988	30
8	Bangladesh Agricultural Development corporation(BADC)	1983-1984	20
9	DANIDA	1982	4
10	BAU	1971-1973	2
11	Housing and Building Research institute(HBRI)	1981	2
12	Bangladesh Academy for rural development(BARD)	1074	1
13	Bangladesh Commission for Christian Development	1078	1
14	Bangladesh Rice research Institute(BBRI)	1983	1
15	Construction partner Organization(CPO)under IDCOL		8,992
	Grand Total	1971-2008	38,765 (Now 19,2008)

Source: Renewable energy and environmental Information network (REEIN), www.reein.org

The various implementing authorities in Bangladesh have limited research and development capabilities and there is limited coordination among the researchers and implementing agencies. That's why most of the plant goes out of order due to the lack of knowledge about maintenance, poor design and defective construction.

2.13 Economics

The cost of waste treatment largely depends on local conditions such as the cost of labour,the availability and cost of materials, land prices, taxes and subsidies and so on (Rahman and Muyeed, 2010). It is fact that the producer of biogas is also the consumer. In this case, they will have to support the overall investments but will

recover the totality of the benefit, and have savings compared to fossil fuels. To be economically viable, there must be a market for the end products. Biogas can be sold or used in almost all parts of the world, where it will offset demand on fossil fuel stocks. The digester liquor is suitable for use as a fertilizer, although frequently supplemental nutrients need to be. Contribution to the prevention of climate change. Environmental factors will also need to consider in economics analysis (Rouf et al, 2003). It is reported by Rahman and Muyeed (2010) that the payback period of 25 properly maintained small biogas plants take between1 and 5 years.

2.14 Previous Study

The study on anaerobic digestion still on research level in Bangladesh. For effective and appropriate designing of a Biogas plant research in different dimension is essential.

Karim, M. A., Professor of the department of Agricultural Chemistry, Bangladesh Agricultural University, Mymensingh, was probably the pioneer in biogas generation from gobar and organic wastes by a pilot plant (Chowdhury and Talukdar, 1978).The generated biogas was used for the chemistry practical classes to burn Bunsen burner and to run photometer.

Chowdhury and Talukder (1978) constructed a commercial family size biogas plant at Thana development center, phulpur, Mymensingh. The biogas plant has a gas storage capacity of about 3cu.m (100 cu.ft) for a 5 to 6 member's family. The gas generated from the plant was used for cooking and lighting at the nearby area of the plant.

Bosu (1993) has done a research work on the effect of mechanical mixing on biogas generation rate. On this work it was also observed that the changing biogas yield due to the variation of dung concentration. In this report it has been showed that reactor with mechanical mixing arrangement increase the gas generation rate.

Rouf et al. (1999) reported the characterization of press mud and its potential for biogas generation. Rouf et al. (2003) has also taken up a study on optimization of biogas generation from press mud in batch reactor. In this study optimization of biogas generation from press mud by mixing with different wastes/residues, and

effects of various parameters has been studied. It has observed in the research work that Press mud when mixed with cowdung the biomethanation process become more stable.

Thangamani et al. (2009) has carried out a study on anaerobic co digestion. On this study tannery waste was used as a substrate by mixing with primary sludge. The potentiality of gas generation of these wastes was investigated there. The studies were carried out in a laboratory with an aim of developing appropriate technology for recovery of bioenergy from the wastes. There Kinetic study of the digestion process was also studied and it has been reported that first order kinetics is adequate to describe this co-digestion process. Volatile solid destruction between 41% and 52%, specific gas production between 0.419 l/g and 0.635 l/g volatile solids feed and methane yield between 71% and 77% were observed there respectively.

Ntengwe et al. (2010) was studied the production of biogas from cow dung, pig and chicken manures and from water hyacinth-cow dung mixture in cone-closed gas collector 1.5 mm thick and 0.7 m wide placed in a brick-walled batch-anaerobic digester 1.5 m deep and 0.8 m wide. The results showed that the pH-temperature-dependent reaction followed the Michaelis-Mentenmechanism which was reduced to First Order kinetics. The pig and chicken substrates produced higher values of yields (3.08 m^3/ton; 3.88 m^3/ton) at pH range of 6.8-8.0 than the cow dung and water hyacinth-cow-dung mixture (0.92 m^3/ton; 0.64 m^3/ton) at average temperatures of 20-27 °C, HRT of 15 days.

Rao and Singh (2004) was carried out a Batch digestion of municipal garbage for 100 days at room temperature(26 ± 4°C; average temperature 25°C)and at ambient temperature (32 ±10°C;average temperature 29°C) conditions for total solids concentrations varying between 45 and 135 g/l. A first order model based on the availability of substrate as the limiting factor was used to perform the kinetic studies of batch anaerobic digestion system. Effect of organic solids concentration and digestion time on biogas yield was studied and mass and energy balance analysis was conducted for batch digestion. The net bioenergy yield from municipal garbage and corresponding bioprocess conversion efficiency over the length of the digestion time were reported to be 12,528 kJ/kg volatile solids and 84.51%respectively. The

methane content of the biogas generated from the reactors was reported in the range of 62–72% with the overall average methane content of the biogas, computed over the total digestion period was 65% by volume.

CHAPTER THREE
AN OVERVIEW OFHAZARIBAGH TANNERY ESTATE, DHAKA

3.1 Tannery Industry in Bangladesh

The consumption of leather products, including leather footwear, within Bangladesh is rather negligible; therefore the bulk of leather produced in the country is exported. The contribution of leather industrial sector in the past decade was around US$ 250 million per year, accounting for around 3% of the country's export (BFLLFEA). Leather occupied the third place among leading export sectors, garments, knitwear and hosiery, frozen foods and jute goods being the first four sectors. The leather industrial sector of Bangladesh has been almost entirely supported by local raw material resources. Based on UNIDO consultants' detailed interaction with the Hide and Skin Merchants Association in December 2005 as well as with a number of tanners and its own assessment, the weight of raw material processed in Bangladesh annually is estimated at present at about 85,000 t/year, with about 48,000 t/year (~56%) belonging to cows, 11,000 t/year (~13%) to buffalo and 26,000 t/year (~31%) to goats and sheep (Nemec, 2010). A specific of the local tanning industry is the Qurbani or sacrifice of domestic animals (typically cows and goats) during the Eidul-Azha festival, which takes place each year. Therefore about 40% of the yearly production of cow hides and goat and sheep skins are available during the Qurbani time and processed within the 75 days following the Qurbani, while the rest of the material is processed during the remaining period of the year. Buffalo hides are available all over the year at a more or less uniform rate. Accordingly the peak load during the Qurbani period (75 days) is estimated at 450 t/day and the load during the rest of the year (225 days), at about 230 t/day (Nemec, 2010). Out of the total 206 tanneries in Bangladesh 192 of them are located in Hazaribagh district of Dhaka city. According to UNIDO (2010) report, small and tiny tanneries are dominant in the total production since 60% of existing production capacity lies in tanneries which produce less than 2 million sq.ft/year.

3.2 Present Status of Hazaribagh

The tannery industry in Hazaribagh, a densely populated area in Dhaka city, is a fitting example of how industrial wastes in some instances can be dangerous and disastrous.Of the 206 tannery units, 90% of them are located on 25 hectares of land in Hazaribagh. The physical look and smell of the area is terrifying and frustrating. There is very little consciousness about environmental protection.

The ancient technological standards that have been set up when the industry was established in the 1960s have remained almost unchanged. In most tanneries safety and health measures are virtually non-existent. According to UNIDO (2010) report, on an average about 15,000 m^3 of highly polluted wastewater generated daily by tanneries in Hazaribagh area is discharged, untreated, into the open channel drains along the roadside passing through the area , which then eventually ends up in the Buriganga river. Often, the drains in the area overflow causing a highly unhygienic atmosphere. Due to the chemicals in the water flocculation takes place, which results in the settling of sludge in channels, which therefore have to be cleaned constantly. The extracted sludge is stored on the sides of the streets and roads. Some scenarios of crude dumping of solid waste of Hazaribagh area are shown in theFigures 3.1, 3.2 and 3.3.

Figure 3.1: Dumped chrome shaving dust **Figure 3.2:** Scattered wastes at the rim of and raw trimming in an open spacea nearby water body

Figure 3.3: Present living conditions in Hazaribagh area

Govt. through the High Court, has ruled that the tanneries should relocate to Savar by February 2010. However, this timeline has since proven to be unrealistic; therefore, the relocation has been extended until 2012. This is mainly because the start of the construction of the CETP has not yet begun, but also because tanneries are not yet ready to move.

3.3 Leather Manufacturing Process

The leather manufacturing process is divided into three sub-processes: preparatory stages, tanning and crusting. All true leathers will undergo these sub-processes. A further sub-process, surface coating may be added into the sequence. The operation flow has to follow the preparatory → tanning → crusting → surface coating sub-process order without deviation, but some of the sub-processes can be omitted to make certain leathers (or partially tanned/ untanned products) (Wikipedia).

Preparatory stages may include

- Preservation- thehide/skin is treated with a method which renders it temporarily unputrescible.
- Soaking - water for purposes of washing or rehydration is reintroduced.
- Liming - unwanted proteins and "opening up" is achieved.
- Unhairing - the majority of hair is removed

- Fleshing - subcutaneous material is removed.
- Splitting - the hide/skin is cut into two or more horizontal layers.
- Reliming - the hide/skin is further treated to achieve more "opening up" or more protein removal.
- Deliming - liming and unhairing chemicals are removed from the pelt.
- Bating - proteolytic proteins are introduced to the skin to remove further proteins and to assist with softening of the pelt
- Degreasing - natural fats/oils are stripped or as much as is possible from the hide/skin.
- Frizing - physical removal of the fat layer inside the skin.Also similar to Slicking.
- Bleaching - chemical modification of dark pigments to yield a lighter coloured pelt.
- Pickling - lowering of the pH value to the acidic region.Must be done in the presence of salts. Pickling is normally done to help with the penetration of certain tanning agents, e.g., chromium (and other metals), aldehydic and some polymeric tanning agents
- Depickling - raising of the pH out of the acidic region to assist with penetration of certain tanning agents (Bienkiewicz, 1983).

Tanning is the process that converts the protein of the raw hide or skin into a stable material which will not putrefy and is suitable for a wide variety of end applications. The principal difference between raw hides and tanned hides is that raw hides dry out to form a hard inflexible material that can putrefy when re-wetted (*wetted back*), while tanned material dries out to a flexible form that does not become putrid when wetted back. A large number of different tanning methods and materials can be used; the choice is ultimately dependent on the end application of the leather. The most commonly used tanning material is chromium, which leaves the leather, once tanned, a pale blue colour (due to the chromium), this product is commonly called “wet blue” (Wikipedia).

Process Description

"Leather tanning" is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather. Production of leather can be done by both vegetable tanning and chrome tanning. Chrome-tanned leather tends to be softer and more pliable than vegetable-tanned leather, has higher thermal stability, is very stable in water, and takes less time to produce than vegetable-tanned leather. Almost all leather made from lighter-weight cattle hides and from the skin of sheep, lambs, goats, and pigs is chrome tanned. The first steps of the process (soaking, fleshing, liming/dehairing, deliming, bating, and pickling) and the drying/finishing steps are essentially the same as in vegetable tanning. However, in chrome tanning, the additional processes of retanning, dyeing, and fat liquoring are usually performed to produce usable leathers and a preliminary degreasing step may be necessary when using animal skins, such as sheepskin.

Chrome tanning in the United States is performed using a one-bath process that is based on the reaction between the hide and a trivalent chromium salt, usually a basic chromium sulfate. In the typical one bath process, the hides are in a pickled state.

Crusting

Crusting is when the hide/skin is thinned, retanned and lubricated. Often a coloring operation is included in the crusting sub-process. The chemicals added during crusting have to be fixed in place. The culmination of the crusting sub-process is the drying and softening operations.

According to Sharphouse (1983),crusting may include the following operations:

- Wetting back - semi-processed leather is rehydrated.
- Sammying - 45-55 %(m/m) water is squeezed out the leather.
- Splitting - the leather is split into one or more horizontal layers.
- Shaving - the leather is thinned using a machine which cuts leather fibres off.
- Neutralisation - the pH of the leather is adjusted to a value between 4.5 and 6.5.
- Retanning - additional tanning agents are added to impart properties.
- Dyeing - the leather is colored.
- Fat liquoring - fats/oils and waxes are fixed to the leather fibres.

- Filling - heavy/dense chemicals that make the leather harder and heavier are added.
- Stuffing - fats/oils and waxes are added between the fibres.
- Stripping - superficially fixed tannins are removed.
- Whitening - the colour of the leather is lightened.
- Fixation - all unbound chemicals are chemically bonded/trapped or removed from the leather
- Setting - area, grain flatness are imparted and excess water removed.
- Drying - the leather is dried to various moisture levels (commonly 14-25%).
- Conditioning - water is added to the leather to a level of 18-28%.
- Softening - physical softening of the leather by separating the leather fibres.
- Buffing - abrasion of the surfaces of the leather to reduce nap or grain defects.

3.4 Solid Waste from Tanning Process

Leather tanning is the backbone of a leather industry which converts raw hide to finished leather. Tanning is a very complex process containing so many steps; Most of the waste fraction from leather industry comes from tanning process. Not each an every step generates solid fraction of waste in the system. To analyze the solid waste it is very important to know the processing system and waste generating steps. The Figure 3.4 illustrates the flow chart of the tanning process and solid waste generating steps.

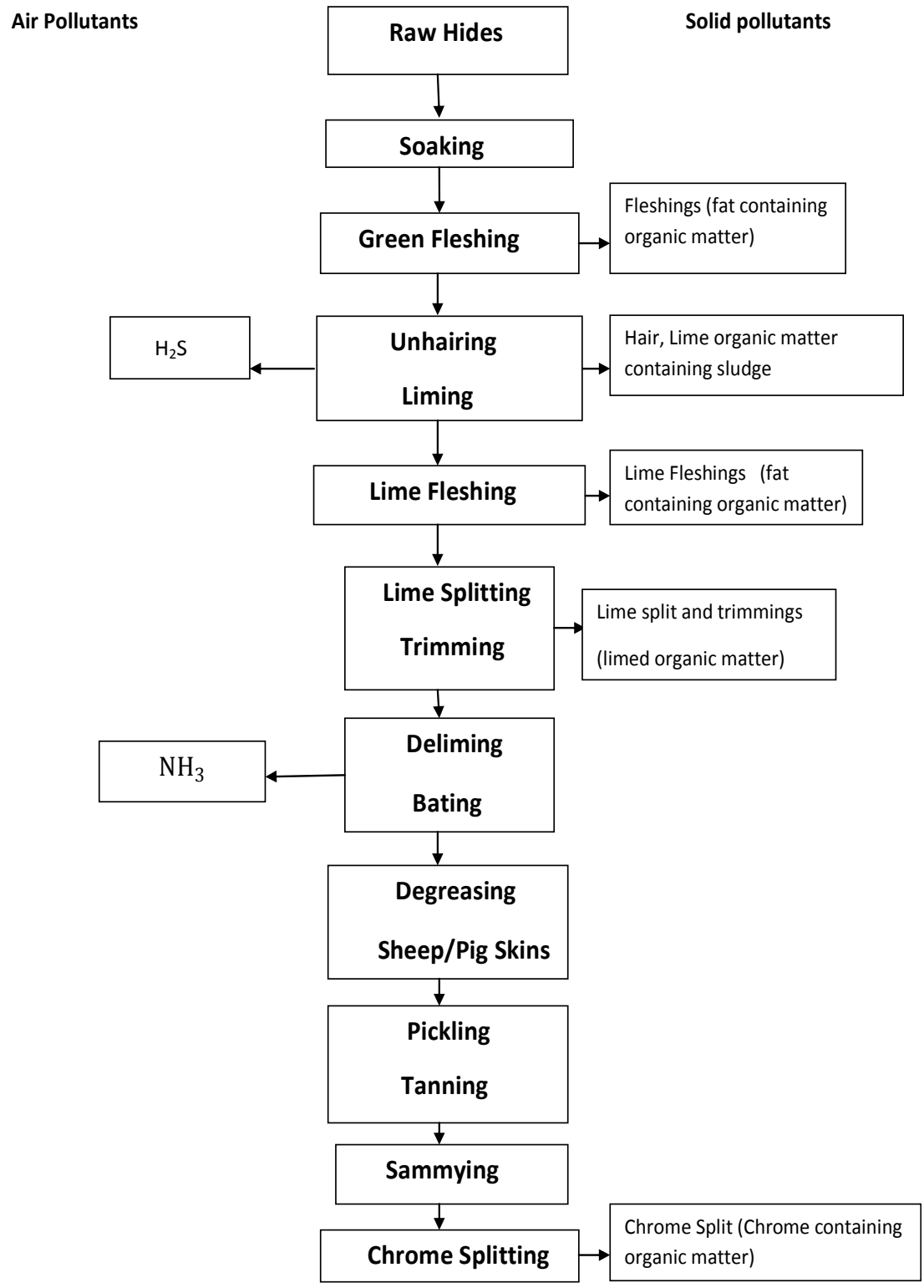

Figure3.4: Process flow diagram of Tanning process

Process flow diagram of Tanning process

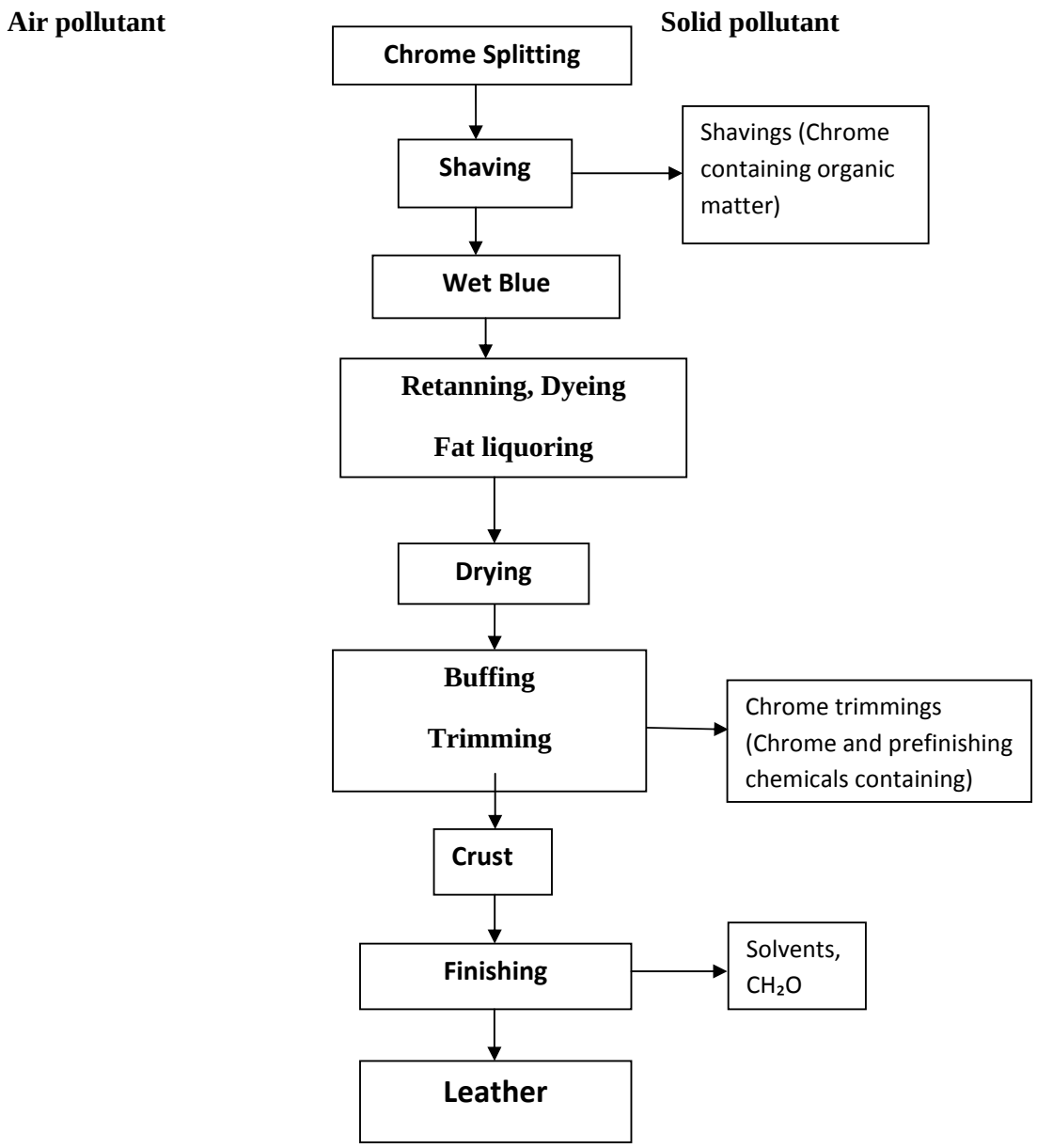

Figure 3.4: Process flow diagram of Tanning process (Continued)

3.5 Solid Waste Sources and Characteristics

The tanning industry is often described as the backbone of the leather industry. It also provides an environmental service for the much larger meat industry as the hides and skins are the by-products of the meat processing industry. In the processing of hides and skins into leather something similar happens. According to Nemec (2010), Tanners' interest lies with the corium or collagen, which represents only about 280 kg out of 1,000 kg of raw hide while all other elements in Figure 3.5 represent wastes.

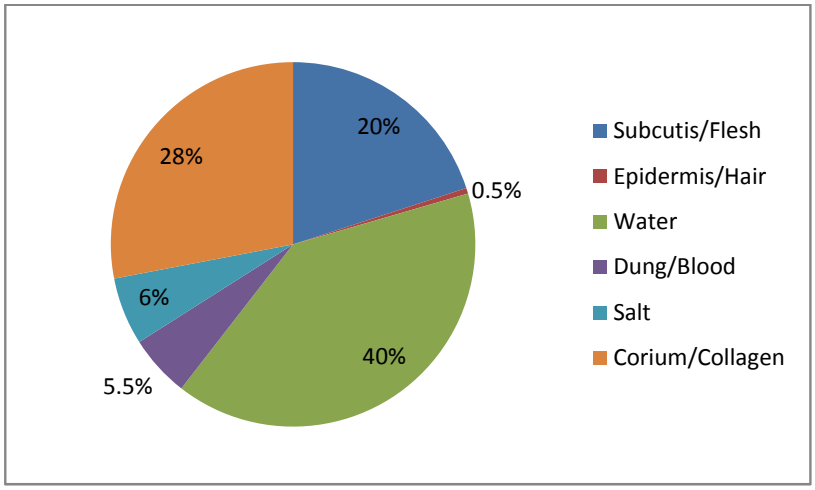

Figure 3.5: Main components of a raw hide or skin prior to processing in a tannery (Nemec, 2010).

3.6 Solid Waste Types and Their Present Management Practices

The main sources of solid wastes in tanneries originate from trimming and fleshing of raw hides and skins as well as splitting and shaving of tanned hides and skin material. However, many of these wastes may be classified as by-products as they may be sold as raw materials to other industry sectors. In different stages of leather processing, various types of wastes are generated from different steps of leather processing. Various pictures of present state of waste management of Hazaribagh area are included in appendix-B. Name of the solid wastes generated in various steps and their present management practices are discussed in Table 3.1.

Table 3.1: Solid waste from various stages of tanning process and their present management practices in Hazaribagh

Types of solid waste	Comments
Dusted Salt	Contaminated with blood, hair, dirt and bacteria. Partly reused in curing and the rest is indiscriminately dumped in undeveloped lands near the tanneries.
Raw Trimmings	The skins are trimmed (especially at legs, belly, neck, and tail parts) in order to give them a smooth shape. The trimmings are usually sold to soap and poultry feed production
Fleshing	This is the flesh material of limed skins. Now-a-days a portion of it is sold to soap and poultry feed makers. Most of the portion is dumped here and there.
Wet Trimming/ Wet Shaving	After chrome tanning, skins or split hides are shaved to proper thickness. This operation produces solid waste containing chrome. Secondary users including poultry feed makers; usually collect these shaving from the tanners.
Dry Trimmings/ Dry Shaving/Buffing Dust	Secondary users, including poultry feed makers, collect cuttings and dry trimmings and buffing dust of the leather from the tanneries.
Assorted Refuse	This is normally sold separately (in bulk) in the retail market.

Source: Field observation, discussion with local people, leather technicians, workers.

3.7 Amount of waste Generated in Hazaribagh

First the solid waste generation estimations for Hazaribagh were calculated using available production data and realistic conversion ratios. To do this properly a distinction was made between hides and skins as the conversion ratios or in other words the relative amount of waste generated from the different operations varies between hides and skins.

Furthermore, a distinction between the Qurbani or peak season (40% of the yearly skins and hides processed within 75 work days) and low or lean season (60% of the yearly skins and hides processed within the remaining 225 work days) is made, as waste generated during peak season needs to be preserved (tanned) and stored so as to allow a more even leather production throughout the year.

The obtained results are shown in Table 3.2, which provides the estimated daily averages generated in Hazaribagh for the different categories of waste depending on the source (hides or skins) and period of production. One can notice the absence of two important waste sources – limed splits and sludge from wastewater treatment. This is because both operations that generate the two types of solid waste are not practiced in Hazaribagh. Furthermore, no hair is currently generated from (bovine) hides since hair-save unhairing is also not practiced.

Table 3.2: Estimated amount of solid waste generated in Hazaribagh based on 2006 Survey

Material	**Unit**	**HIDES and SKIN average Generation**	
Season		**Lean**	**Peak**
Wet salted raw hides/skins	t/day	230	450
Raw trimmings	t/day	11.5	22.5
Hair (pasting)	t/day	3.3	7.7
Fleshing	t/day	20.6	40.5
Wet blue trimmings	t/day	6.6	13.6
Chrome splitting (bovine)	t/day	4.9	8.9
Chrome shavings	t/day	16.1	31.5
EI/crust shavings*	t/day	3.5	6.8
Buffing dust*	t/day	1.2	2.4
Dyed trimmings*	t/day	1.4	2.7
TOTAL	t/day	69.1	136.6

* Assumption: 50% up to crust and 20% of total production up to finished leather.

Source: Nemec, 2010

The Table 3.3 illustrates the amount of different types of waste generated from per ton of raw leather processing in different tanning industry.

Table 3.3: Measured amounts of solid waste generated in several tanneries in Hazaribagh in 2010

Tannery Name	HIDE				SKINS
	Apex	Bay	Karim	Average	Lien
From Raw to Fleshing:					
Salt (kg/t)	8.7	3.2	5.1	5.6	11.5
Raw trimmings (kg/t)	83.1	43.9	48.5	58.5	96.5
Limed fleshings* (kg/t)	215.3	135.0	113.6	154.6	392.1
From Wet Blue processing:					
Splits (kg/t)	244.6	181.2	201.4	209.1	0.0
Chrome shavings (kg/t)	92.7	75.2	74.6	80.9	57.0
WB trimming (kg/t)	40.3	8.2	12.7	11.7	57.8
From Crust processing:					
Buffing dust (kg/t)	11.5	7.2	7.2	8.7	0.0
Crust trimmings (kg/t)	19.8	13.9	13.6	15.8	28.8

* The amount of limed fleshingshas been calculated as the difference in weight of pelts before and after fleshing.

Source: Nemec, 2010

3.8 Solid Waste Management Options

Residues from tanneries can be tradable products, non-hazardous waste or hazardous waste. The classification, re-use, recycling and disposal depend on the legal context in the respective country, as well as on the availability of markets and facilities for treatment and re-use/recycling. The situation differs broadly among countries around the World. It is true that currently many residues are being disposed of, generally in landfills, as this is the cheapest option. According to Nemec, 2010 best practices for waste management and treatment involve evaluating the options in order of priority:

- prevention
- reduction
- re-use / recycling / recovery
- disposal

Due to high investment costs many treatment options are not economically feasible on a small scale (for individual tanneries). However, TED offers the opportunity for tanneries to share off-site treatment plants or to transport residues to treatment plants as a complement to other wastes. Wastes coming from tanneries require careful handling because many residues are contaminated by chemicals, infectious materials and odors also. Therefore, in order to make an efficient waste management option, it is important to first separate specific waste fractions to prevent or at least reduce the degree of contamination of waste to a bearable level. Then need to apply the best possible method for managing each portion of waste.

CHAPTER: FOUR

MATERIALS AND METHODS

4.1 Introduction

The methodology of this research work can be divided into four parts. The first part of the study included field visit, to find out the whole picture of the study area it was required and the relevant secondary data and some questionnaire survey information have been included in the previous chapter. In the second part of the study samples were collected and analyses of the sample's different properties were done simultaneously. Then the preparation of substrate followed by experimental setup of small scale anaerobic digestion unit had been done. Finally, continuous monitoring and data collection were performed for analyzing the method.

4.2. Selection of the raw materials

4.2.1 Tannery waste

Leather processing is characterized by large amounts of solid and liquid waste. Pretanning processes are those in which most of the solid waste is produced. The viable substrate for biogas production produced in tannery industry is waste fleshings which is solid waste, composed mostly of lipids and fats. They originate from the process of animal skin preparation for the tanning process. In this process all adherent flesh and fatty tissue is removed from animal skin and rough edges and impurities of skin are also removed, becoming waste. In order to examine the appropriate technology for the management of solid waste from tanning industry it is necessary to assess the full tanning process and the characteristics of the waste.

By examining the present management practices and the chacteristics of waste, one ofthe vital solid wastes fractions of tannery industry, fleshing has been chosen to be used as substrate for biogas generation. Fleshings are shown in Figure 4.1.

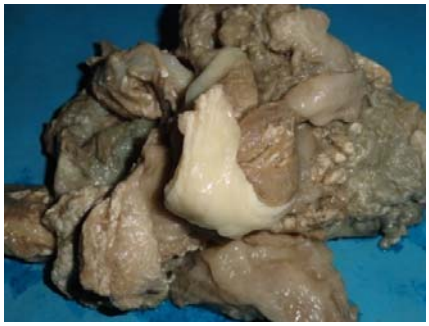

Figure 4.1: Raw fleshing

4.2.2 Domestic sewage and cowdung

Domestic sewage was chosen as diluent to maintain the solidfleshings in suspension and to achieve the desired level of flow ability in the feed mixture. Domestic sewage would also act as a source of various microorganisms required for anaerobic digestion process. As C/N ratio of fleshing material was quite low for using them directly as substrate for gas generation, to increase the C/N value and to maintain the high pH of fleshing cowdungwas used with fleshings in different proportion in the digestion process. Though the C/N ratio can also be increased by adding cellulose powder as it is a source of carbon but that was not done. Because cowdung not only increases the C/N value of the substrate but also act as a buffering media in the digestion process (Rouf et al, 2010).

4.2.3 Inoculum

Pre-digested material consisting of all the essential microbes (hydrolyzing, fermentative, acetogenic and methanogenic bacterial consortium) has been chosen as an inoculum for the study. The inoculum was synthesized in the laboratory using cowdung by 6% TS concentration and water in the prevailing environmental condition.The working volume of that slurry was one liter. After cessation of gas production, the digested residue was used as inoculums for the study to initiate digestion.

4.3Sample collection and preparation of substrates

Fleshingswere collected from three types of local tannery (Small-Medium-Big). The domestic sewage samples were collected from different locations of elephant road residential area (from open drain) and the cowdung samples were collected from a

nearby firm. All the raw materialswere collected at different time and stored at 4^0C, before analysis and other experiments. The raw materials were characterized by analysis, with Standard Methods (APHA, 2000).All the analytical values (For fleshing and domestic sewage) have also been included in table A-4. Among them one of the samples for each of the raw material was selected randomly for preparing feed stock. The limed fleshing used as substrate was grounded to less than 6-mm diameter using a table knife. To this, domestic sewage was added as diluent in 1:1 ratio (Fleshing: Sewage). Cowdungwas also mixed with fleshing and domestic sewage in different proportion to maintain the C/N ratio of the slurry of the different reactors.

4.4 Experimental Setup of Anaerobic Digestion Reactors

In order to examine the appropriate technology for the management of solid waste from tanning industry, anaerobic digestion process has been studied using four batch reactors. A simple methanogenic activity test procedurewas adopted (Isa et al, 1993; Jawed and Tare 1996). The characteristics of limed fleshing, Domestic sewage and Cowdung used in the batch experiments has been described in Table 5.1.

Three glass bottles were used for each of the experimental setup of a batch reactor. One bottle was for slurry, the second one was filled up with water to collect gas, and the last one was vacant.A known amount (6% solids) of substrate containing a mixture of waste was transferred into 2-litre capacity wide mouth glass bottle. This is the first bottle and these first bottles containing slurry in all the setup were closed by rubber stoppers. All the three bottles in each setup were connected with each other by plastic pipe. The second bottle was sealed by rubber cork with two way glass stop cork. Of the two ways on the stop cork one was for connecting first and second bottle by a plastic pipe as shown in figure 4.2 and the other way was for releasing gas from second bottle. When one of the ways was in function the other way was remain closed. Generated gas from the first bottle comes through the pipe to the second bottle and creates pressure on the water of the second bottle and then due to the pressure of gas the water from this bottle goes to the third bottle through the connected pipe between them. In this way by the water displacement method the generated gas was collected in the second bottle and the gas production rate was

recorded from the scaling of the second bottle. When the second bottle was filled up with gas, the gas was released through the other way of the stop cork. At that moment the third bottle was placed in an elevated place so that by the gravity force the water of the third bottle can create back pressure on the gas of the second bottle and then by the pressure of water the gas is released through the other way of the stop cork. The experimental set up of the reactors in the laboratory is shown in Figure 4.2.

Different proportion of waste materials were mixed and added to the glass bottle to obtain a working volume of the 1 litre for all the reactors. After mixing all the raw materials the slurry of reactor R3 is shown in Figure 4.4. All the reactors contained 6% solids, it was chosen because usually 6% solid concentration gives optimum biogas yield (Rouf et al, 2010). For reactor R1, on 6% solids of the slurry it contains 50% of cowdung, and fleshing and domestic sewage 50%, then to fulfill 1000ml, tap water was added after addition of 100ml inoculums. Similarly,In R2 reactor, it contains 25% ofcowdung and 75% of fleshing and domestic sewage, the remaining portion is filled up with inoculums and tap water. In reactor R3, it only contains Fleshing and domestic sewage that is 100% and others remaining the same. The fourth and last reactor R4 contains only 12.5 % of cowdung on 6% solids of the slurry. The fleshing and domestic sewage were mixed by 1:1 basis in all the reactors.The summary of the reactors on the basis of their contents are given below:

Reactor R1: 6% solids [Cowdung (50%) + Fleshing and Domestic sewage (50%)] + Inoculum (100ml) + Water (Amount required to be filled up 1000ml) = 1000ml

Reactor R2: 6% solids [Cowdung (25%) + Fleshing and Domestic sewage (75%)] + Inoculum (100ml) + Water (Amount required to be filled up 1000ml) = 1000ml

Reactor R3: 6% solids [Cowdung (0.0%) + Fleshing and Domestic sewage (100%)] + Inoculum (100ml) + Water (Amount required to be filled up 1000ml) = 1000ml

Reactor R4: 6% solids [Cowdung (12.5%) + Fleshing and Domestic sewage (87.5%)] + Inoculum (100ml) + Water (Amount required to be filled up 1000ml) = 1000ml

In all the reactors fleshing and domestic sewage were mixed by 1:1 basis and the total volume of the slurry was 1000 ml.

The composition of slurry in different reactors in wet weight basis (w/v) is described in the Table 4.1. The amounts were taken by rounding up the figures that achieved after calculation for easy handling.

Table 4.1: Quantity of limed fleshing, domestic sewage, cowdung and inoculums indifferent reactors.

Reactors Name	Fleshing (g)	Domestic Sewage (ml)	Cowdung (g)	Inoculum (ml)	Tap water (ml)	Volume of the slurry (ml)
R1	125	300	180.0	100	295	1000
R2	170	450	90.0	100	190	
R3	225	600	0.0	100	75	
R4	195	525	45.0	100	135	

The total gas production was measured using a water displacement method at an interval of 24 h. Contents of the glass bottle were mixed manually, after every gas measurement. Daily gas production was recorded. Using water displacement method gas releasing or burning of produced gas is shown in Figure 4.3. The entire test was conducted at a temperature of 30 ±3°C for a period of 60 days.

In the month of August to October, first month was required for the preparation of inoculum. Room temperature, pH of the effluent are also monitored routinely. From the second week VS reduction and COD reduction was measuredat the end of every 10 days throughout the experiment.

Steady-state condition is identifiedwhen the COD value of the effluent and daily biogas productionis measured to be the same for two or three consecutive days.

Figure 4.2: Experimental Setup of the reactors in the laboratory

Figure 4.3: Gas Burning

Figure 4.4: Slurry of Reactor R3

Figure 4.5: Slurry after digestion

4.5 Process parameters

Some of the commonly used anaerobic process indicators include pH, chemical oxygen demand (COD) destruction, volatile solid (VS) destruction, volatile fatty acid (VFA) concentration, gas production and gas composition.

Most of the indicators listed above have been reported as appropriate for evaluating the effect of organic loading rate on the bioconversion of organic substrates (Thangamani et al, 2009) and hence, these Parameters have been chosen for assessing the decomposition of the substrate investigated in this study. Only volatile fatty acid concentration could not be measured due to lack of lab facilities.

4.6 Analyses

Characteristics of different substrates were determined through extensive laboratory analysis. The parameters were determined included pH, total solid, and volatile solid, moisture content, protein content, C: N ratio, oil content and COD values. Further the effluent slurries were also analyzed. In this case, the parameters were determined included pH, volatile solids and COD values of the slurry of different reactors throughout the digestion period. The composition of produced gas was also analyzed.

pH was measured electrometrically. Digital pH meter (HANNA, HI 98204) was used for the determination of pH of the samples. Two buffer solutions containing pH 4.0 and 7.0 were used to calibrate the digital pH meter. Carbon and Nitrogen contents of the fleshings, domestic sewage were determined by the help of a C-H-N elemental analyzer. Moisture contents were estimated by gravimetric methods by drying at 105^0C. The protein content was estimated from the nitrogen content by multiplying with 6.25.Calorific value was determined according to IS: 1350(Part 4)-197 by bomb calorimeter.

Total solids (TS) and Volatile solids (VS) were estimated according to the procedures recommended in the Standard methods for examination of water and waste water (APHA, 2000). Volatile solids were determined by drying at 550°C for 1hour at furnace. Oil content was determined by soxhlet extraction method. Potassium dichromate was used to determine COD values of the samples. A thermometer of range 0–60 °C having an accuracy ±0.5 °C was used to measure room temperature. Assay bottles were periodically analyzed for the above-mentioned parameters for a period of 8 weeks. Gas production from the reactors was monitored by means of water displacement method on daily basis. The volume of water displaced from the bottle was equivalent to the volume of gas generated at the temperature and pressure that prevailed during the study period. The total methane content present in the gas was evaluated by Orsat gas analyzer. The analysis method by orsat analyzer has described by Vogel (1961).

The apparatus consists essentially of a calibrated water-jacketed gas burette connected by glass capillary tubing to two or three absorption pipettes containing chemical solutions that absorb the gasses it is required to measure. Concentrated sodium hydroxide was used as absorbents. The base of the gas burette is connected

to a levelling bottle to enable readings to be taken at constant pressure and to transfer the gas to and from the absorption media. The gas is then passed into the sodium hydroxide burette, left to stand for about two minutes and then withdrawn, isolating the remaining gas via the stopcock arrangements. The process is repeated to ensure full absorption. After leveling the liquid in the bottle and burette, the remaining volume of gas in the burette indicates the percentage of carbon dioxide absorbed. The remaining portion of the gas mixture is methane.

4.7 Experimental Procedures and Sampling Schedules

A known quantity of wastes was added in a bottle as an initial experiment when it gave remarkable result then measured quantity ofraw materials corresponding to each volatile organic load was added in four bottles after evaluating the substrate composition. Thus, the test reactors for four different organic loading were constructed. At the end of every 10^{th} day, the slurry sample was collected from each of the bottle andvarious parameters were analyzed. Phase contrast and biogas generation was observed by photographic documentation.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Introduction

Fleshing is a type of animal tissue waste generated during the preparatorystages of leather processing in relatively larger quantities as compared to other types of solid waste in the tanning industry (Thangamani et al, 2009). Fleshing contains a significant portion of biodegradable matter which is suitable for recover of energy from it. Leather industry is one of the leading export oriented sector in our country. But improper and unhealthy management of waste of this industry, has now became a concerning issue in the context of environment. The studies were carried out in a laboratory scale reactor with an aim of developing an appropriate technology for recovery of bioenergy from the waste of tannery industry and subsequently ensure their safe disposal so that it can be an eco friendly option for leather industry.

5.2 Characteristics of Raw Material

Characteristics of the raw materials used for the study are given in Table 5.1.The table shows that fleshings contain 82.57 % volatile solid and considerable amount of oil that is 9.50 % (dry basis). It also contains protein of 44.16 %. The C/N ratio of fleshing is 2.64, which was quite low for optimum biogas generation (Rouf et al, 2010) and that low C/N valuewas increased by mixing with cowdung and domestic sewage. Low C/N value substrate when mixed with high C/N ratio substrate the slurry performs better (Rouf et al, 1999). The pH of the fleshing is extremely high for its liming effect and that is 10.99. Buffering capacity of cowdung is very good and the domestic sewage would also act as a source of various micro organisms required for anaerobic digestion (Thangamani et al, 2009). The characteristics of cowdung, domestic sewage and inoculums are also shown in the Table 5.1.

Table 5.1: Characteristics of Substrates

Constituents	**Limed Fleshing**	**Domestic Sewage**	**Cowdung**	**Inoculum**
pH	10.99	6.15	6.21	6.43
TS (%)	13.38	5.0	17.0	6.0
VS (%)	82.57	82.0	89.0	88.6
Oil (%)	9.50	2.32	1.56	-
Protein (%)	44.16	25.32	7.89	-
Moisture Content (%)	86.62	95	83.0	94.0
COD(mg/l)	-	1329	-	-
CalorificValue(Kcal/kg)	4323.06	4010.04	4658.07	-
C/N Ratio	2.64	20	24.0	-

5.3 Biogas Generation

5.3.1 Daily gas production

The Figures 5.1 to 5.4 represent the volumes of daily gas accumulation with varying amount of fleshing in different reactors. The observed data of daily gas generation in four reactors are presented in Table A-1 in appendix A. Belt shape trend of daily gas generation of reactor R1 (VS conc.55.33 g/l), where fleshing and domestic sewage was 50% on 6% solids of the slurry, is shown in Figure 5.1. It was observed that gas generation started at the very next day of charging the digesters with the slurry. The rate of gas generation gradually increased with increasing the digestion period.In this reactor, the peak gas production of 1100 ml was observed on the 34^{th} day. It was observed that gas production rate declined after 54^{th} days.

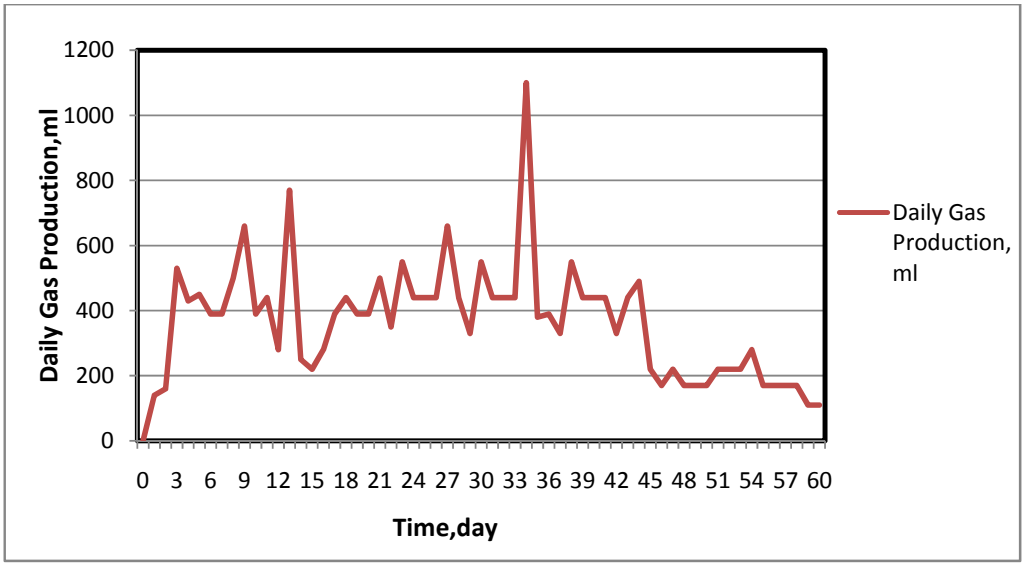

Figure 5.1: Daily gas production and time in reactor R1

Considerable amount of daily gas generation for R2 reactor (VS conc. 52.45g/l), which contains 75% of fleshing and domestic sewage, is shown in Figure 5.2. Quite frequent sharp shape of daily gas production is showing by the graph. In this reactor also the generation of gas started from the second day after recharging the reactor with slurry. The peak gas production was observed on the 28th day, the amount was 1100 ml.

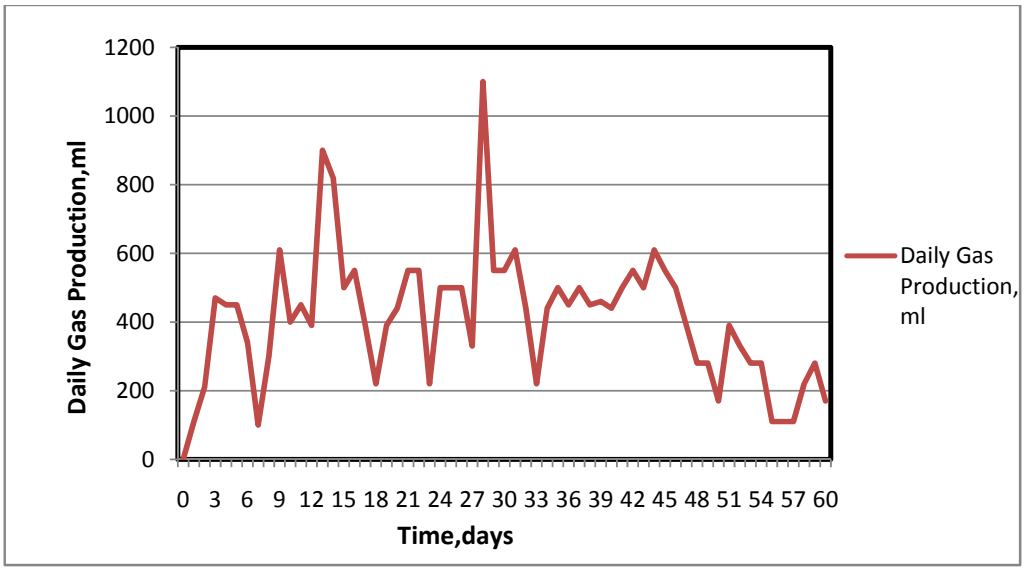

Figure 5.2: Daily gas production and time in reactor R2

Figure 5.3 represents the daily gas production rate for reactor R3 (VS conc. 50.80 g/l), which contains 100% fleshing and sewage on 6% total solids. This shows lower range of daily gas production (100-300ml). As there was no cowdung in the slurry and the inoculums was used in the slurry originate from cowdung based biogas unit so that in the other reactor the cowdung gets all the necessary microbes for gas generation. For this reason, in this reactor the gas generation was started from the fourth day after setting up the reactor. The peak gas production was observed 550 ml at the 23rd day of digestion period.

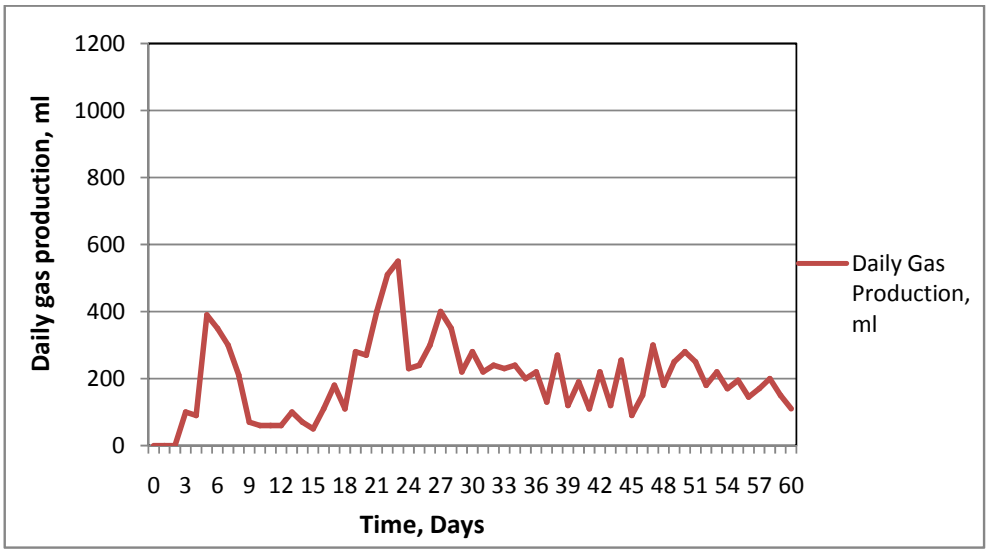

Figure 5.3: Daily gas production and time in reactor R3

The daily gas production rate in R4 reactor (VS conc. 51.56 g/l) is shown in the Figure 5.4.R4 reactor consists 87.5% fleshing and domestic sewage of the total solids of the slurry. In this reactor also the generation of gas started at the second day after charging the reactor. The peak gas was 780 ml which was observed at the 26th day. The gas generation also ceased at the 60th day of digestion period. A gradual shift was observed in the period of peak gas production with increasing VS concentration.

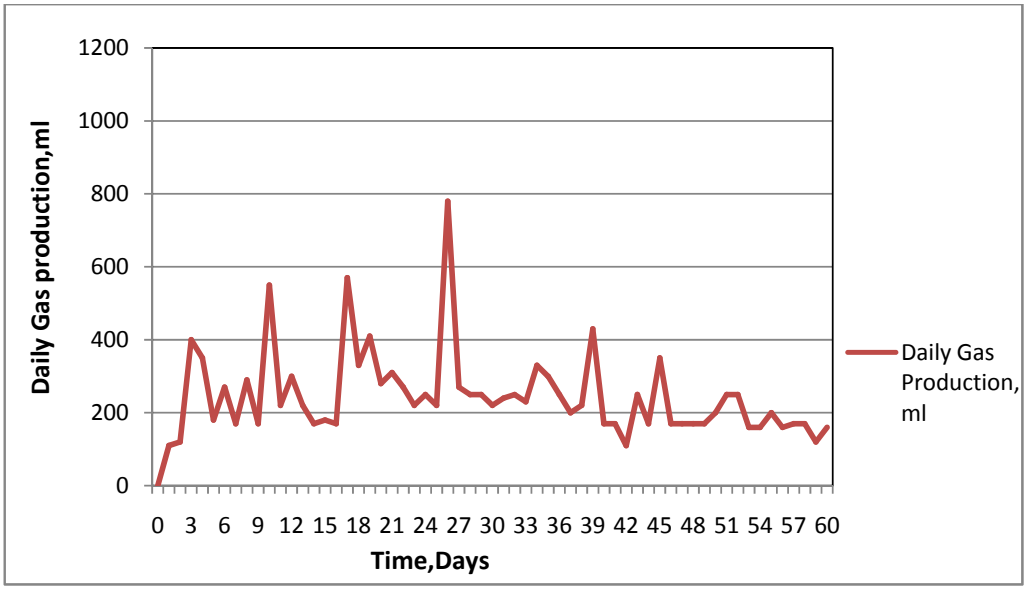

Figure 5.4: Daily gas production and time in reactor R4

The relation between periods of peak gas production with initial volatile solid concentration of different reactors is shown in Figure 5.5. It was observed from the value of daily gas production of different reactors that peak gas production in a reactor occurred earlier when the volatile solids concentration of the reactor was lower. The higher the initial volatile solid concentration, the more time was required for peak gas production of the reactor.

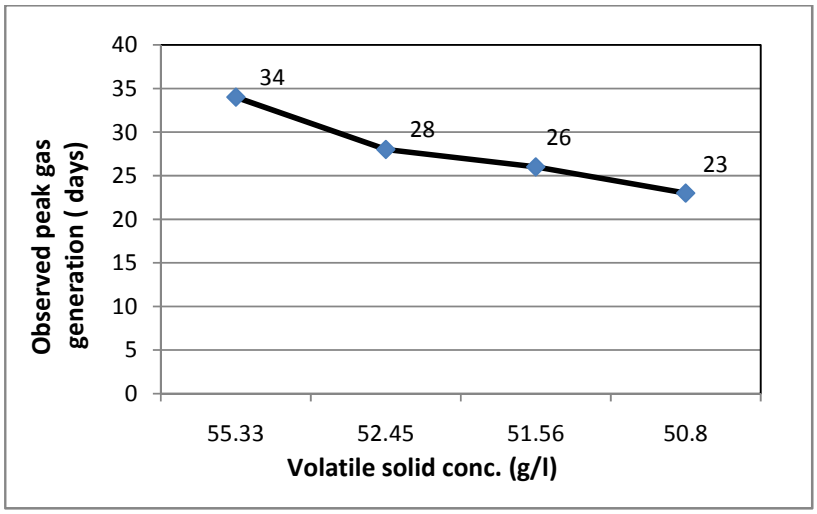

Figure 5.5: Relation between period of observed peak gas generation (days) with initial VS concentration of four reactors

5.3.2 Cumulative Gas Production

The cumulative gas production from each of the test reactors operating at various organic loading of tannery solid waste, domestic sewage and cowdungis shown in Figure 5.6. The calculated data of cumulative gas production are shown in Table A-2 in appendix A. A cumulative gas production from test reactor R1 (VS concentration of 55.33 g/l) was 22,200ml at the end of the eighth week of the study period. A cumulative gas production from the test reactor R2 (VSconcentration of 52.45g/l) was 24,960 ml while a cumulative gas production of 12,145ml was observed in test reactor R3 (VS concentration of 50.80 g/l). In the last and fourth reactor R4 (VS concentration of 51.56 g/l) cumulative gas production was observed 14,850 ml. Figure 5.6 shows that the lag phase prevailed upto 5 to 6 days of digestion period This was due to microbe limiting at the initial stage of fermentation. After the lag period, the cumulative volume of gas increased sharply and continued upto 50 to55 days of fermentation period. After which the rate of gas generation decreased and this declination continued until the gas generation almost ceased. At the end of sixty days of digestion period gas generation in all the reactors almost ceased.

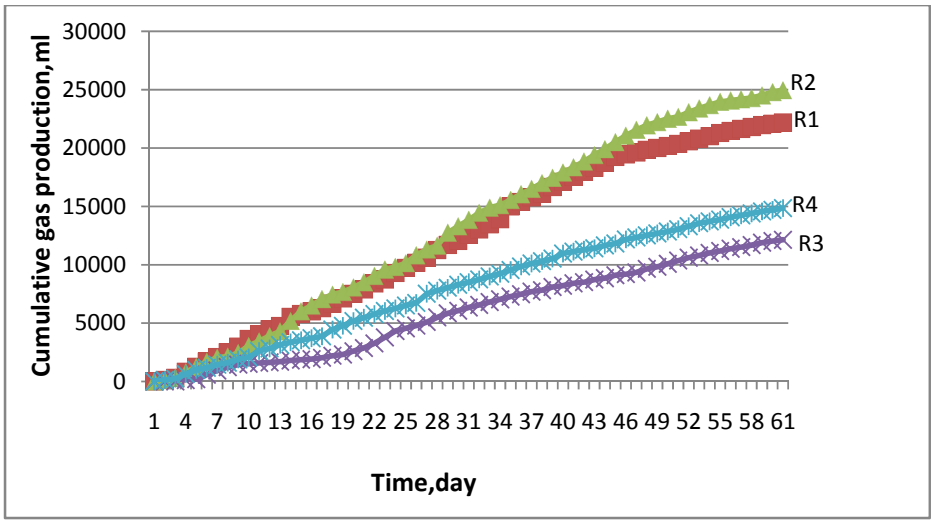

Figure 5.6: Cumulative gas production in different reactor

The Figure 5.7 represents the variation of cumulative gas production at different time. The Figure shows that in all the reactor highest gas was generated after 20 days of digestion period. In the first and last 10 days of digestion period generation of gas was low. For the reactor R1and R4, highest gas was generated in 30thto 40th days

whereas in reactor R2 and R3 the highest gas generated in 20thto 30th days of digestion period.

The Figure 5.7 also shows that highest gas was generated from reactor R2 and in most of the digestion period gas generation rate was higher for R2 reactor than others. Even though R2reactor contained less amount of cowdung than R1 reactor, there also gas generation rate was higher. It was observed that, fleshing's potentiality of gas generation is more than using cowdung in anaerobic digestion.

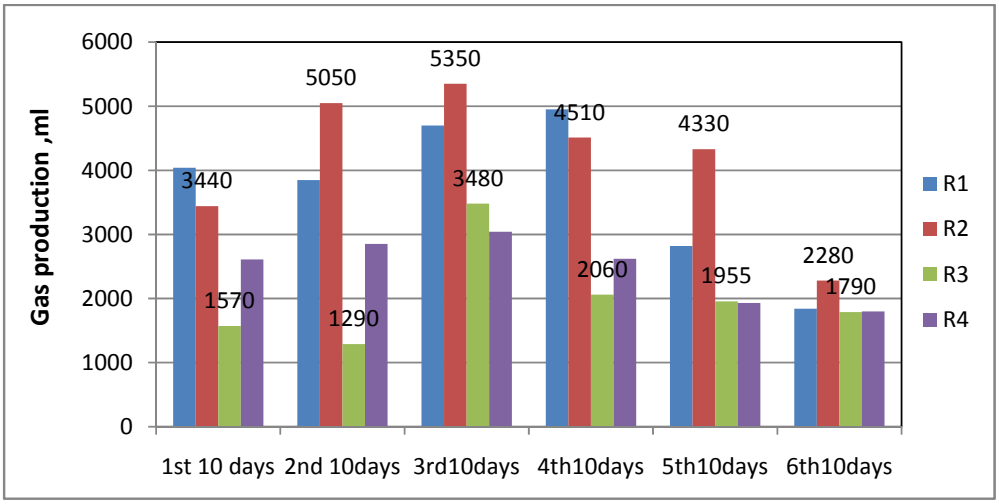

Figure 5.7: Variation in biogas production at different time at different reactor

5.4 VS destruction in batch reactor

During anaerobic digestion of solid waste, biogas generationis more specifically related to reduction of biodegradablefraction of VS in the digester. VS reduction in the test reactors was observed in the range of 41–52%. These valuesare comparable with the VS reductions reported in the literaturefor various substrates (Rouf et al, 2010; Thangamani et al, 2009). The percentages of volatile solids of slurry decreased with increasing digestion period. The results of linearity for volatile solids with respect to time are given in Figure 5.8. The percentages of solids are highly correlated with the digestion time as the values of R^2 are about 99% for all cases. The tendencies of concentrations for solids are decreasing as negatively sloped trend curve are shown in Figure 5.8. The experimental results of volatile solids concentration in different digestion period are presented in Table A-5 in appendix A.

The degree of reduction depends on the initial volatile solids concentration of the slurry (Bosu, 1993). Biogas generation is a biological process and bacteria consume carbon for cell building and energy source extracting from solids which causes solid reduction.

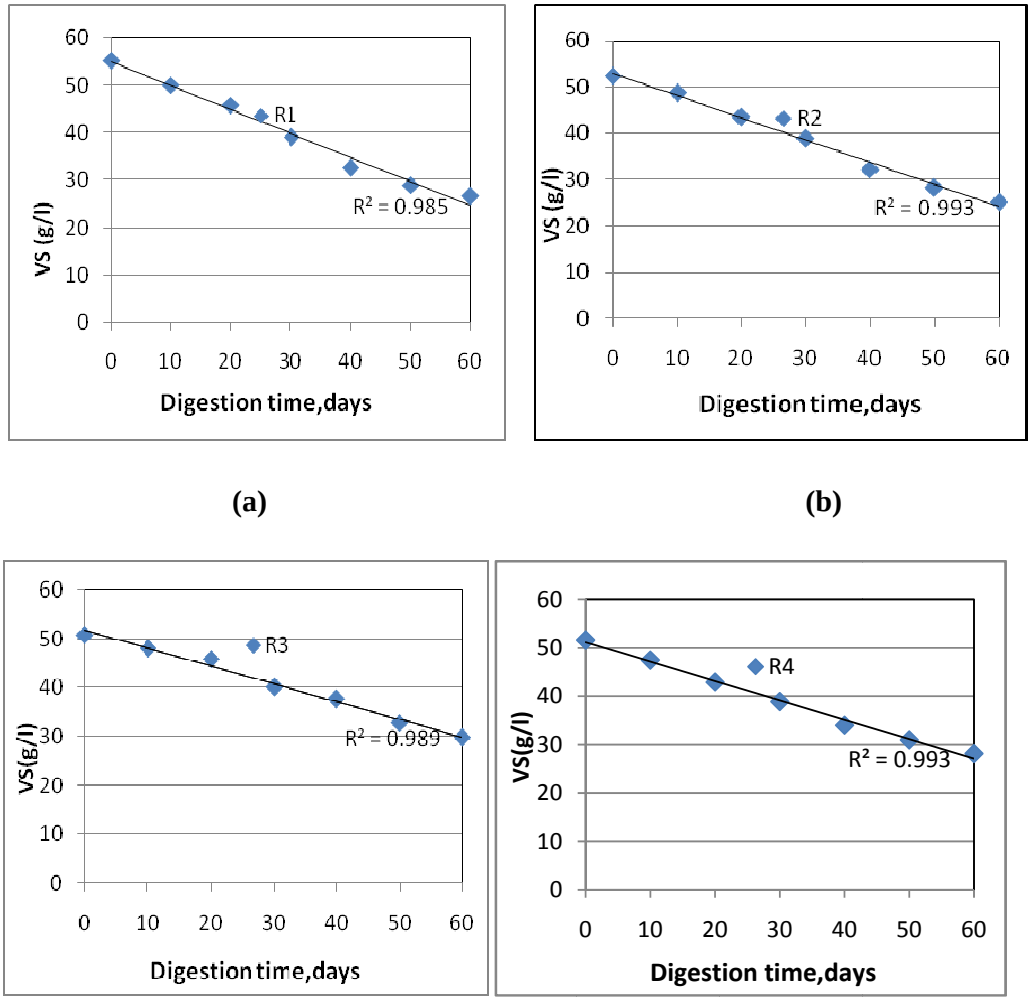

Figure 5.8: Trend curve of Volatile solids (VS)

Figures 5.9, 5.10, 5.11 and 5.12 illustrate the variation of VS destruction and cumulative gas production in the four reactors R1, R2, R3 and R4 respectively. Specific gas production in terms of volatile solid fed was 0.401, 0.476, 0.239 and 0.288 l/g respectively.The specific gas production obtained was comparable with the trends reported by Thangamani et al. (2009). All the relations between gas generation and volatile substrate degradation are shown in Figure 5.9 to 5.12. It is

found that the gas generation rate according to the degraded volatile solids was higher in R2 reactor than other three reactors.

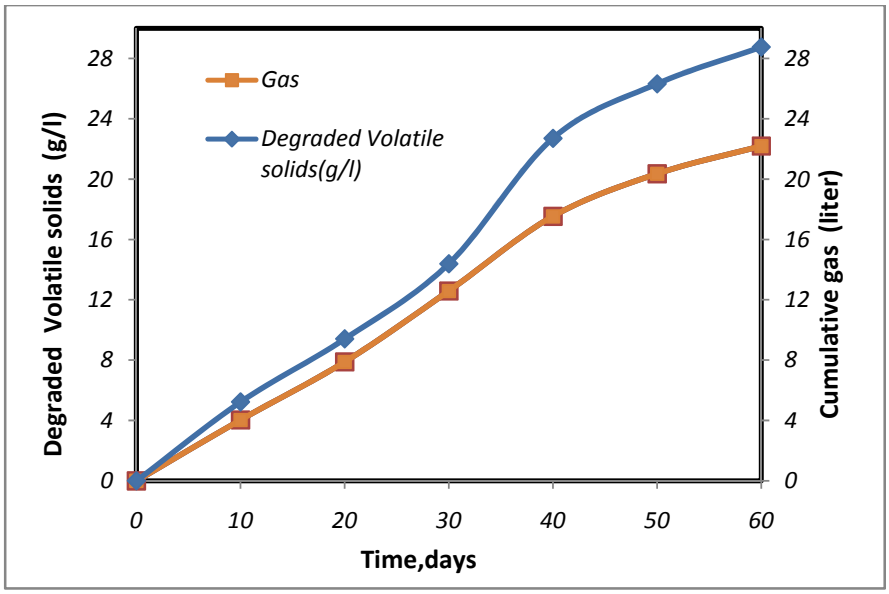

Figure 5.9: VS destruction and cumulative gas production with time in R1 reactor

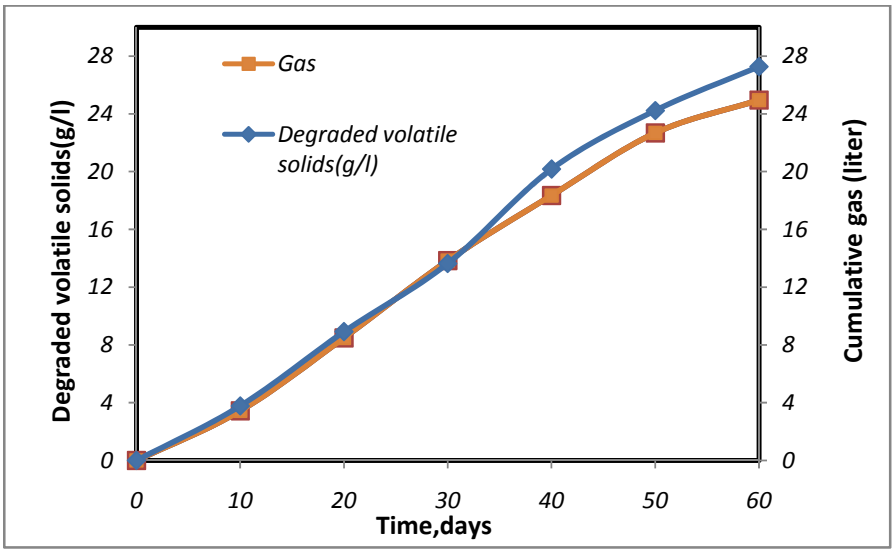

Figure 5.10: VS destruction and cumulative gas production with time in R2 reactor

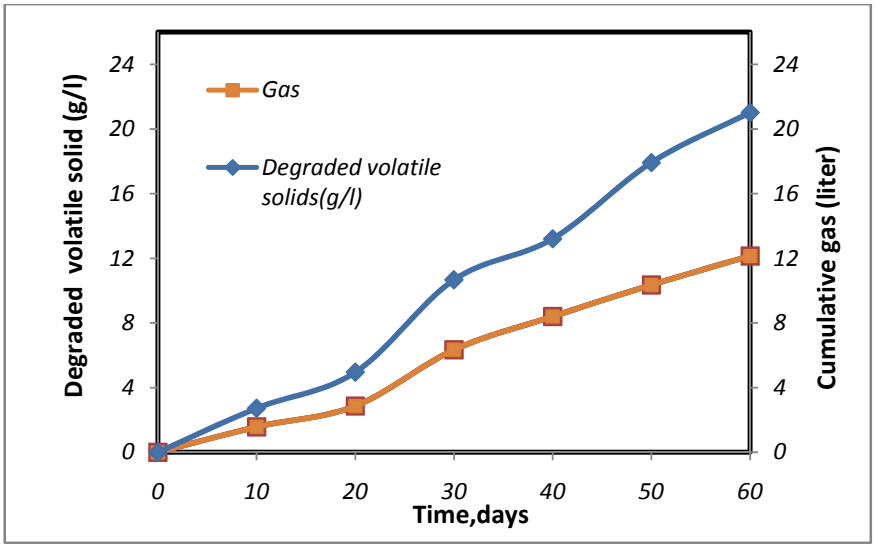

Figure 5.11: VS destruction and cumulative gas production with time in R3 reactor

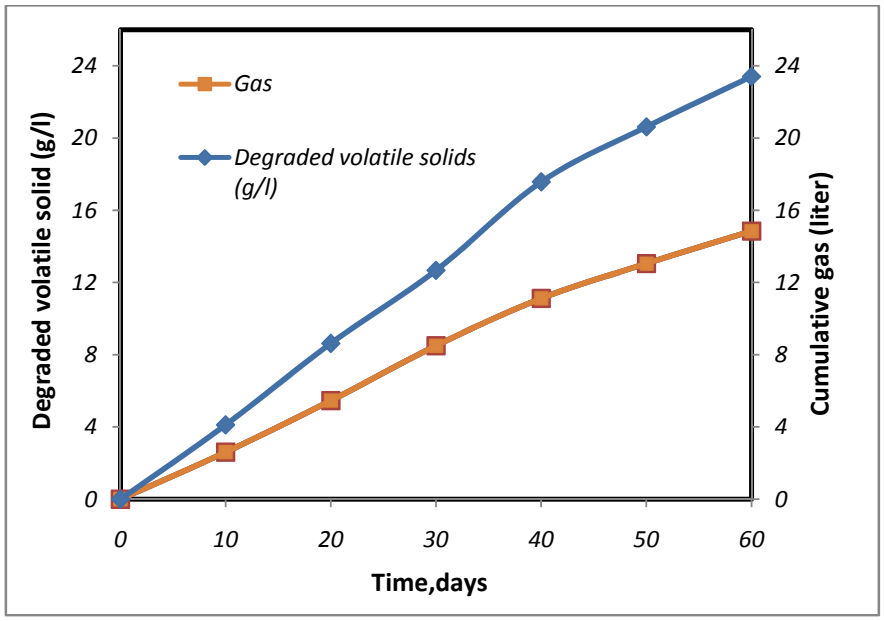

Figure 5.12: VS destruction and cumulative gas production with time in R4 reactor

The initial and final values of volatile solids concentration and volatile solid reduction in different test reactors and the yield constants are shown in the Table 5.2.

Table 5.2: Change in VS concentration in the reactors and yield constant of different reactors

Reactor	VS(g/l)		VS reduction (%)	Yield of gas generation(l/g)
	Initial	Final		
R1	55.33	26.57	**51.97**	**0.77**
R2	52.45	25.18	**51.99**	**0.91**
R3	50.80	29.78	**41.38**	**0.58**
R4	51.56	28.15	**45.40**	**0.63**

The values of VS destruction indicate that in the R3 reactor, which contained 100% fleshing and domestic sewage on 6% total solids of the slurry, the volatile solids destruction rate was lower than other three reactors. As there was no cowdung in the reactor R3 to seed the process with bacteria and fleshing was the major source of biogas on that slurry. On the other hand in R2 reactor, which contained 25% cowdung with 75% of fleshing and domestic sewage on 6% total solids of the slurry, 52% volatile solids reduction achieved there. This indicates that VS reduction rate not only depends on initial concentration but also on types of volatile matter of the slurry .The specific gas yield was higher in R2 reactor than the other three reactors. The results draw attention to that amended fleshing with sewage was not very much suitable for optimum gas generation but when fleshing was mixed with cowdung and domestic sewage in appropriate proportion, it presented the best performance.

5.5 COD Value reduction

Chemical oxygen demand (COD) of the slurry considerably reduced by anaerobic digestion process. The reduction of COD value means the reduction of pollution load from any substrate by the treatment process. The COD value trend curves for four different reactors are shown in Figure 5.13. The trend line shows that good correlation exist between digestion time and COD value as the R^2 value is above 95% for all the reactors.

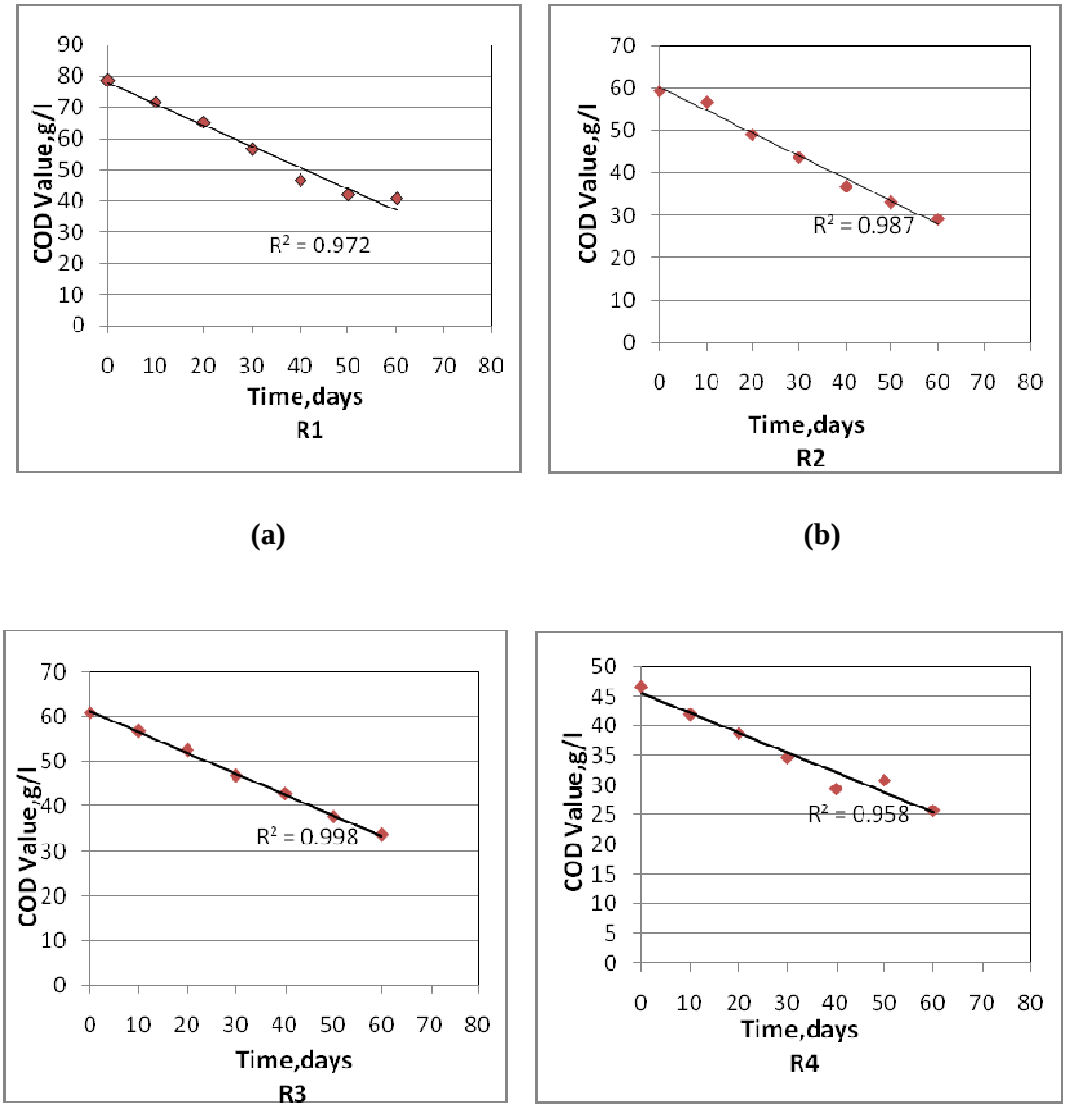

Figure 5.13: Trend curve for COD value for different reactors

For reactor R1 48.02% COD reduction achieved, for R2, R3 and R4 COD reduction rate was 50.67%, 44.80% and 44.61% respectively. Maximum COD reduction achieved from reactor R2 where maximum gas was produced. COD reduction value is comparable with the reference value given by Rahman and Muyeed (2010). The amount of methane generation from conversion of a unit mass of a substrate depends on the composition of the feed materials. Depending on the feed considered, 1 g of biomass can be equivalent to different amount of COD; The COD/VS mass ratio of the substrate then determines the amount of methane generated from the conversion

of 1gm of volatile solid of the substrate. The COD/VS ratio of the 6% substrate was found to be:

Amount of methane generated from 1g VS degraded = Methane generated from reduction of 1g of COD × (i); i= COD/VS. The calculated values of i for reactor R1, R2, R3 and R4 were found 1.31, 1.10, 1.30 and 0.89 respectively.

5.6 Effect of cowdung concentration

The variations in volume of gas production with different percentages of cowdung used in the slurry of different reactors are given in Figure 5.14. In the total solids of the slurry of a reactor a certain amount of cowdung was used to initiate gas generation. As the initial pH of the fleshing was so high, the cowdung also used as a buffering media and seeding material. In reactor R3, as there was no cowdung, lag time of 5 days was observed before the onset of maximum gas generation in this reactor. This might be because of more time required by the fleshing to break up and to participate in gas production and in other cases cowdung participated in gas production more rapidly due to the presence of inoculums originated from the cowdung based biogas unit. From the performance of the four reactors, it can be concluded that optimum gas generation took place when 25% of total solids of the slurry of a reactor was cowdung. A significant impact on gas production rate was also observed due to the use of varying amount of cowdung in four different reactors.

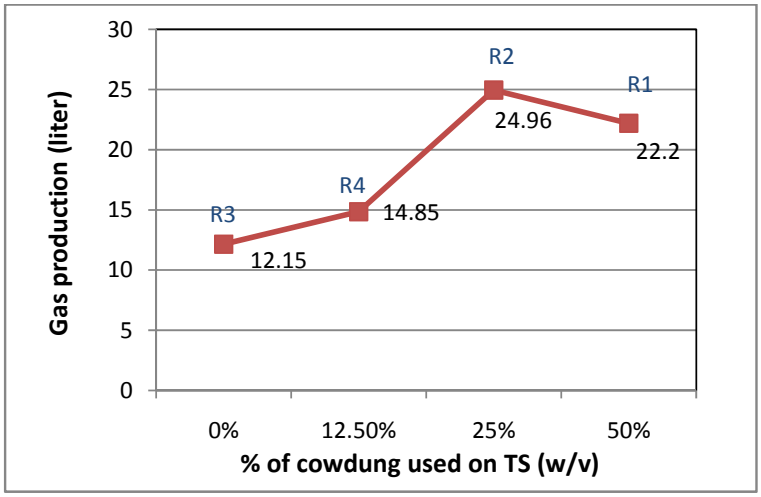

Figure 5.14: Effect of cowdung on gas production

5.7 Effect of temperature

The digestion period was 60 days from September to October in this study. The climate was hot and dry in the study period. As there was no special arrangement to maintain the optimum temperature (35°C according to Bosu (1993)) for gas generation. The room temperature prevailed during the digestion period. That was 30°C ± 3 throughout the period. The temperature chart is given in Table A-3 in appendix. It was noticed that when temperature increased the gas production also increased. This confirms the dependency of biogas generation on temperature. After 20 days from the startup of the reactors, sudden drop of temperature (almost 5°C) occurred in the study period. According to Seadi (2001), gas generation might be ceased due to the sudden drop of temperature. But it was observed that the test reactors were run as usual in this study. The reason may be that the reactors were in establish condition and the bacteria were already acclimatized themselves with the environment there. For this reason, the sudden fall down of temperature did not hamper the gas generation. Due to the limitation of the reactors configuration the slurry temperatures have not been measured in this study.

5.8 Effect of pH

The pH is another important process monitoring parameter for anaerobic digestion. According to Rahman and Muyeed (2010), the desirable pH range is between 6.5-8.0 for anaerobic digestion process and the highest gas yield was observed by the Chengdu Research Institute was 7.5 to 8.0. pH profiles for all the reactors are shown in Figure 5.15 to 5.18 respectively. In Figure 5.15 the gas generation in R1 reactor was observed at pH ranges of 6.8 to 7.15. Initial pH level of the slurry of all the reactors reduced because in an anaerobic process, the acid former bacteria active at first and substrate converted to acid quickly and as a result pH was decreased. Then because of the activities of methanogenic bacteria the volatile acids converted to methane and carbon dioxide and pH increased again. The following reactions might be taken place in the test reactors:

Hydrolysis **Acetogenic bacteria**

$$\text{Cellulose} \longrightarrow C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH\ (\text{acetate}) + 2CO_2 + 4H_2 \qquad (5\text{-}1)$$

Methanogenic bacteria

$$CH_3COOH\ (\text{acetate}) \longrightarrow CH_4 + CO_2 \qquad (5\text{-}2)$$

$$CO_2 + H_2 \longrightarrow CH_4 \qquad (5\text{-}3)$$

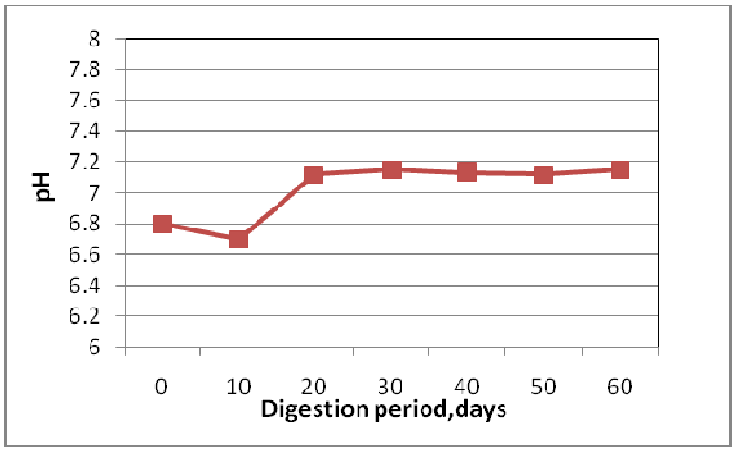

Figure 5.15: pH profile for R1 reactor

Gas generation was observed in the pH range of 7.0 to 7.2 for the R2 reactor. pH profile for R2 reactor is shown in the Figure 5.16.The highest gas production was for the pH range of 7.0 to 7.20 for R2 reactor. This value is comparable with the literature values.

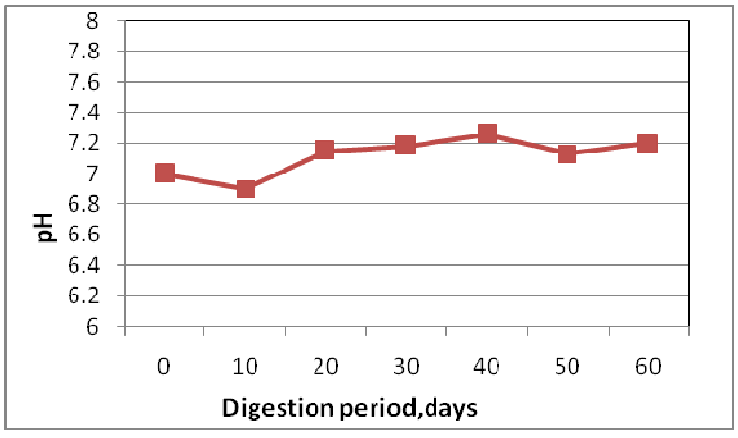

Figure 5.16: pH profile for R2 reactor

pH profile for R3 reactor is shown in Figure 5.17. Gas production was observed at pH ranges of 8.61 to7.3 for R3 reactor. Initial pH for R3 reactor was quite high but that was buffered by the process itself.

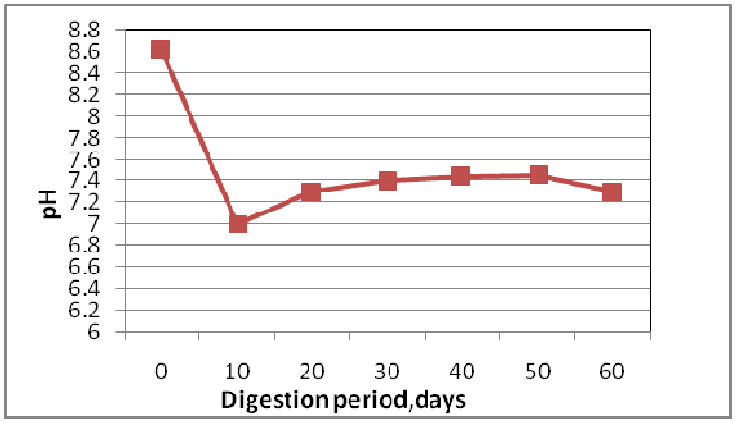

Figure 5.17: pH profile for R3 reactor

pH profile of reactor R4 is shown in Figure 5.18. Gas generation was observed at pH ranges of 7.49 to 7.32 for R4 reactor.Stability of pH is very important for a process run; it was observed that which was quite maintained in all the reactors by the process of the reactor itself.

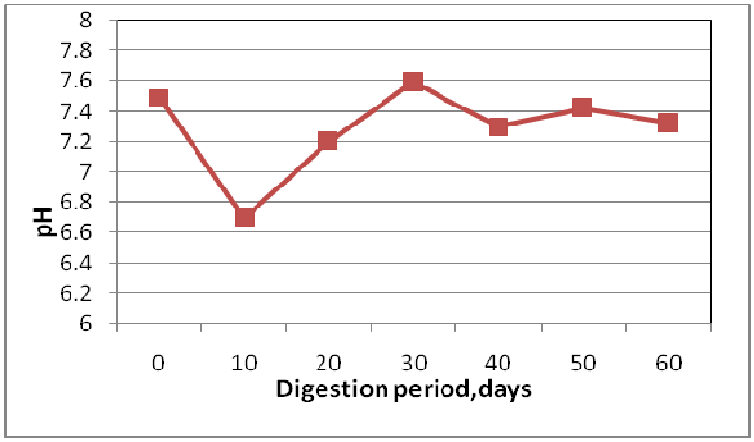

Figure 5.18: pH profile for R4 reactor

5.9 C/N ratio

Biogas yield (based on initial total solid concentration) at different C/N ratio of four reactors are shown in Figure 5.19. The C/N ratio offleshing material was very low that was 2.64. Generally low C/N ratio of a substrate indicates the high protein contents of the substrate. In an anaerobic process the excess protein degrades to NH_3. Elevated concentration of NH_3 may create toxicity for anaerobic bacteria and the process may be inhibited. For this reason cowdung and domestic sewage has been used as co-substrate to maintain the C/N ratio of the substrates. The reactors were operated at C/N ratio of 18, 17, 15 and 16 respectively which were little low from standard value (20 to 30) (Rahman and Muyeed, 2010).But in this range reactors operated without any setback even at lowest C/N value of R3 reactor was given considerable amount of gas. Biogas yield at optimum C/N ratio was 0.416 l/g in reactor R2.

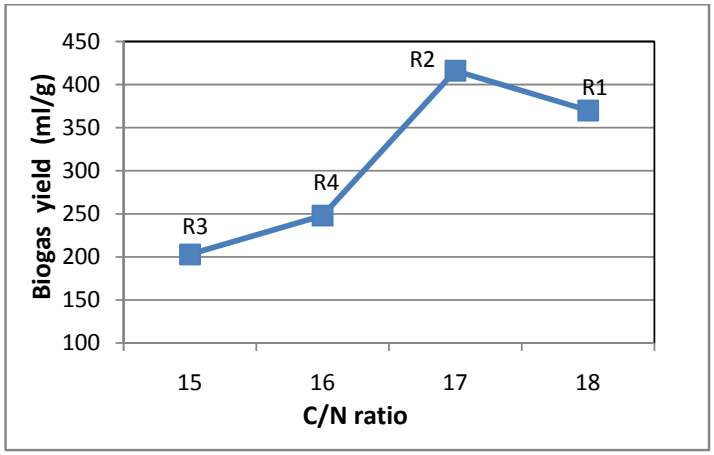

Figure 5.19: Biogas yield at different C/N ratio

5.10 Gas Composition

Biogas from anaerobic digestion usually contains 60% $CH_4$and 30-35% $CO_2$and a little percentage of trace elements, generally H_2S. Gas composition was measured several times as it confirms the quality of produced gas. The composition of produced gas for all the reactors is shown in Figure 5.20 to 5.23 respectively. All the data are presented in tabular form in Table A-9 in appendix A also. In the first seven days of digestion period all the analysis showed lower percentage of methane content

than CO_2 content. The reason is that initially long chain polymeric molecules were converted to smaller chain molecules and then converted to different volatile acids. During this process some CO_2 were produced. In addition to this, the CO_2 from degradation of acetate to methane also added to the produced gas and increased the percentage of CO_2 in the gas composition. After 20 days of digestion period CH_4 content wasincreased considerably and it was continued until gas generation stopped. Due to lack of laboratory facility only CO_2 and CH_4 content was measured to know the gas composition, other trace elements were not measured. The higher percentage of methane was observed in all the reactors because of the reaction takes place in the slurry are as follows:

$$NH_3 + H_2O \longrightarrow NH_4OH \qquad (5\text{-}4)$$

$$NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 \qquad (5\text{-}5)$$

In this way CO_2 remained in water and as a result CH_4 content increased.

The Figure 5.20 shows the percentages of methane and the carbon dioxide content of the produced gas of reactor R1. The methane content in reactor R1 was 48.5% to 72.1% by volume.

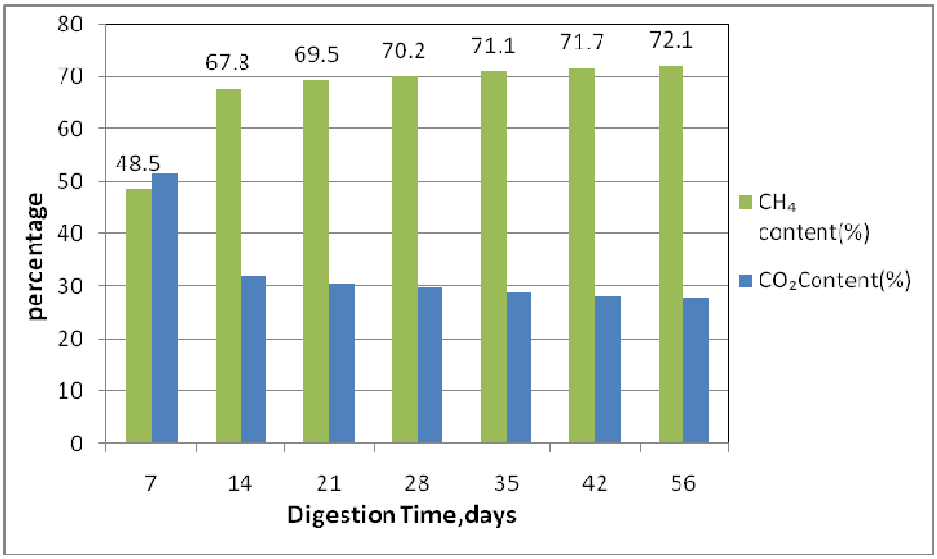

Figure 5.20: Variation of gas composition with time in R1 reactor

The gas composition of reactor R2 is shown in the Figure 5.21. For R2 reactor the methane content range was 47.4% to 72.6% by volume over the digestion period.

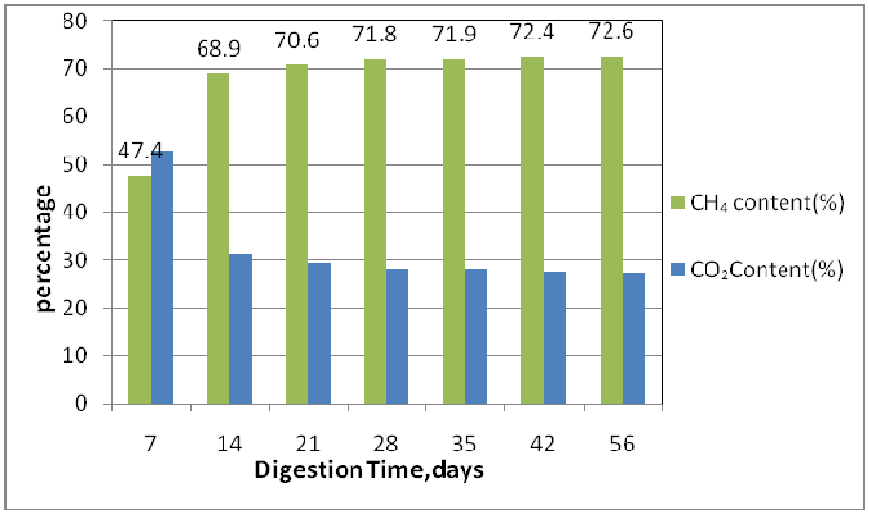

Figure 5.21: Variation of gas composition with time in R2 reactor

The gas composition of R3 and R4 reactor are shown in Figures 5.22 and 5.23 respectively. In R3 reactor the methane content was 46.5% to 70.4% by volume and in R4 the range was 46.4% to 71.6% by volume.

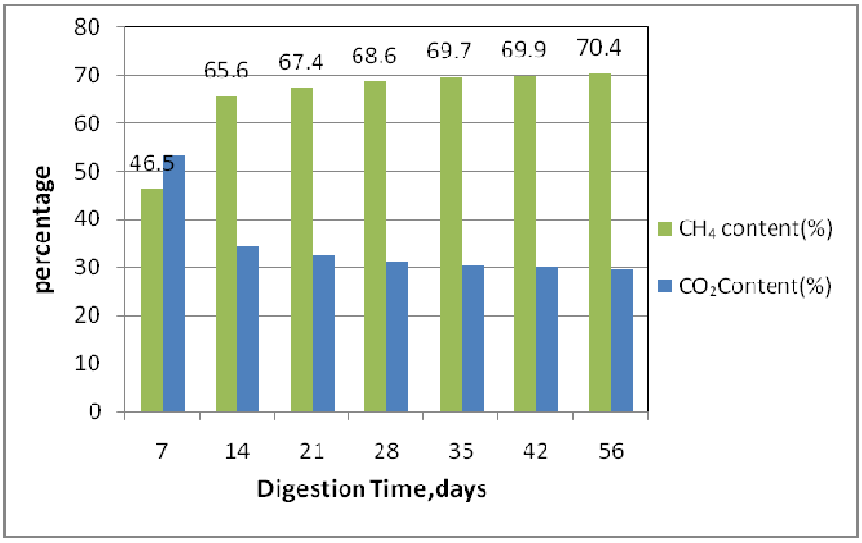

Figure 5.22: Variation of gas composition with time in R3 reactor

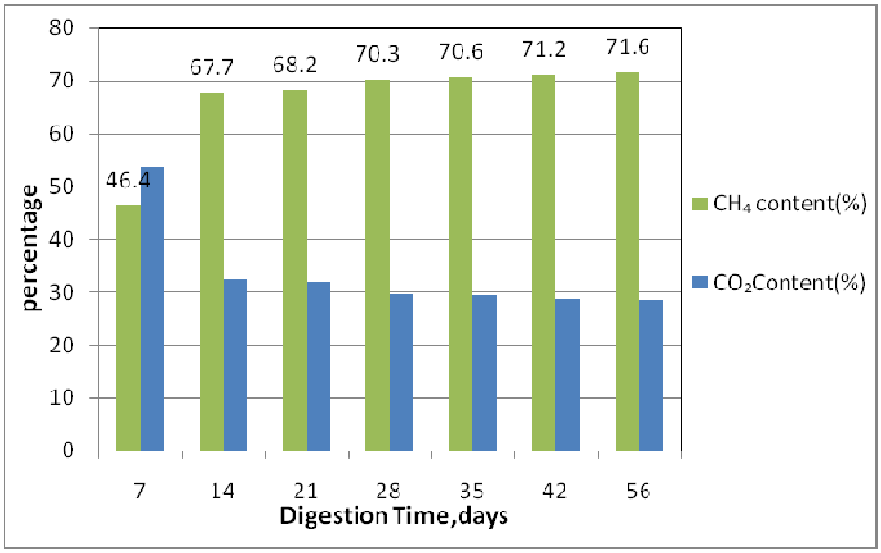

Figure 5.23: Variation of gas composition with time in R4 reactor

Almost similar trendof gas composition was observed (in Figure 5.20 to 5.23) for different reactors. Rounding up the figures it can be concluded that methane content for R1, R2, R3 and R4 reactor were 72%, 73%, 70% and 72% by volume respectively, which were significant values to consider them as clean fuel. Reactor R2 consist the highest methane yield which was remarkable.

5.11Biodegradability of feed mixture

All the volatile matters in the slurry are not biodegradable especially lignin. As the tannery solid waste fleshings originates from animal skin this may contain lignin. The refractory fraction in the feed mixture is an indicator of the extent of biodegradability of the substrate. It is the portion (may include lignin) of initial VS that remains in the digester as solid retention time (SRT) approaches infinity (Borja et al, 1995).The refractory fraction was determined graphically from the intercept of the plot drawn between (S/S_o) and $(S_o*t)^{-1}$ where S=substrate concentration (g/l), S_o= initial VS concentration (g/l) and t = retention time (d) (Thangamani et al, 2009). The biodegradability of feed mixture (refractory fraction) was determined from the intercept. Though the scattered points of the graph were fitted well with the second order polynomial but according to the experimental value the intercept value in the second order polynomial was very low. For this reason straight line was fitted for the scattered point to find out the refractory fraction. It was in the range of 37–51% of

the influent volatile solids concentration (Table A-8). The biodegradability factor obtained from the graph indicates the presence of resistant volatile matter is the major portion of volatile solids in the digester. This reasonably conforms to the experimentally determined VS destruction efficiency of 41–52% in Table 5.3 (Parawira et al, 2004). Hence, it is essential to monitor the biodegradable fraction of volatile solid in the feed to have better operational control over the process. The graphical model presentations for determining refractory fraction of different reactors are shown in Figure 5.24, 5.25, 5.26 and 5.27 respectively.

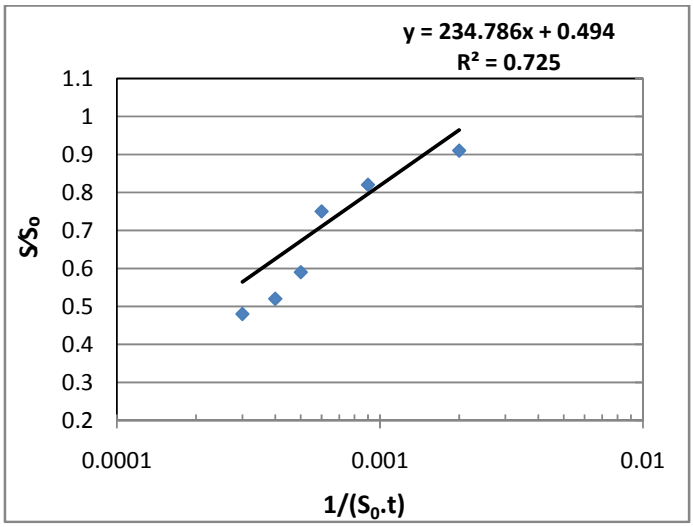

Figure 5.24: Refractory fraction in reactor R1

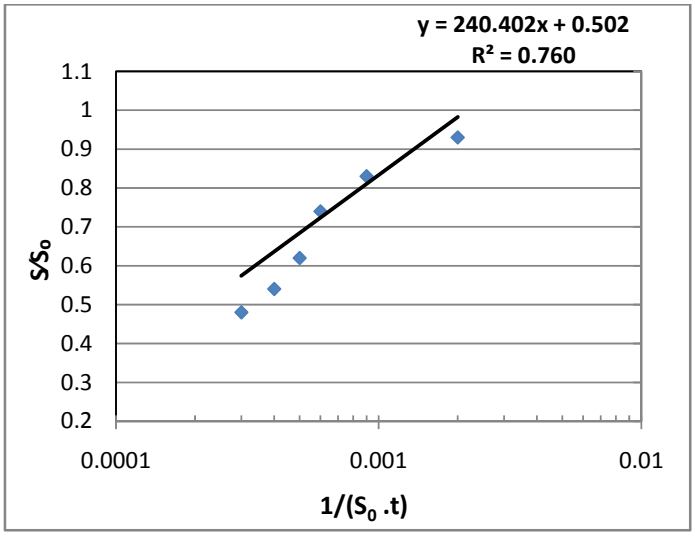

Figure 5.25: Refractory fraction in reactor R2

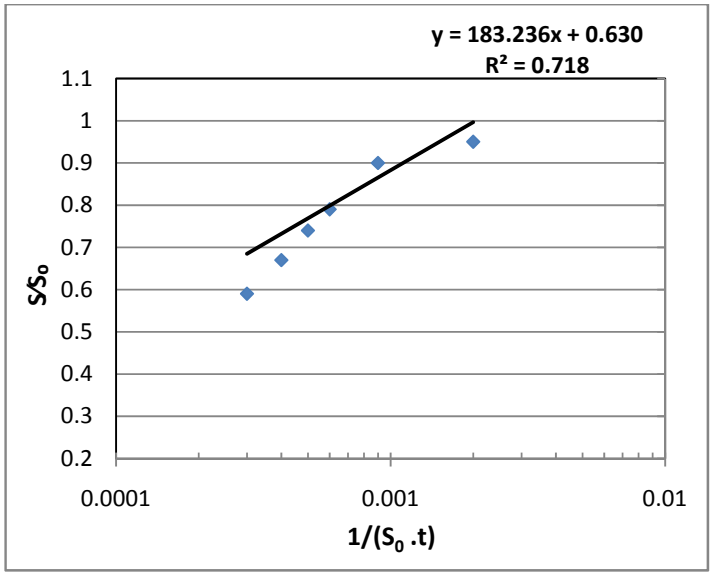

Figure 5.26: Refractory fraction in reactor R3

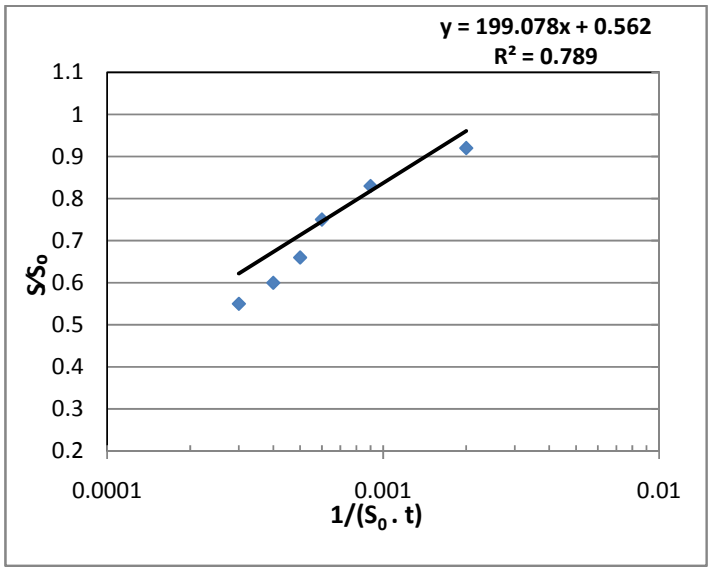

Figure 5.27: Refractory fraction in reactor R4

The biodegradable fraction of volatile solids obtained from graphical model and the experimental values are presented in Figure 5.28 to evaluate the accuracy of the model. The values are also presented in tabular form in Table A-5 in appendix A.

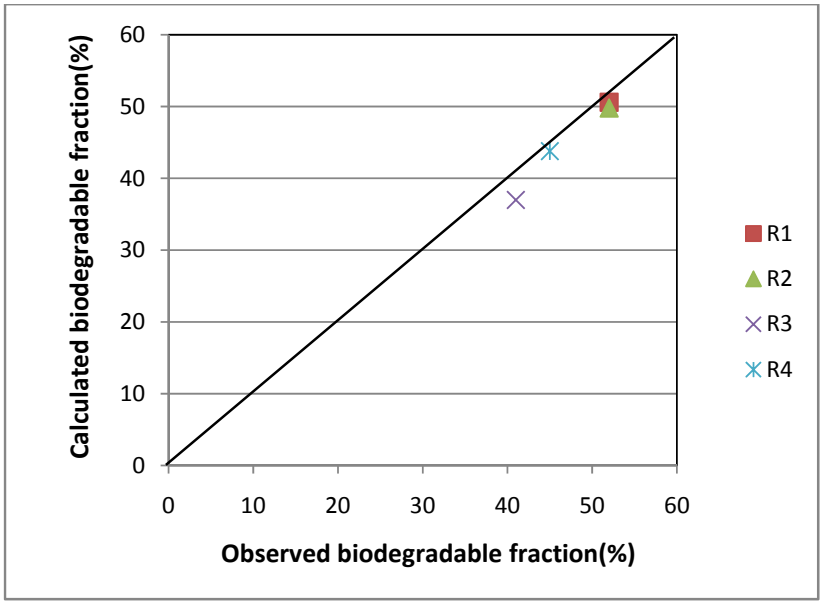

Figure 5.28: Verification of graphical model

5.12 Kinetic Analysis

Anaerobic digestion process is generally described by the first order kinetic model, which is based on the following two factors (Mahmud et al, 2004; Parker, 2005):

(1) The rate of substrate conversion to biogas is directly proportional to the substrate concentration and

(2) The volume of gas generated is proportional to the mass of the substrate destroyed

The corresponding kinetic equations are:

$$dS/dt = -kS \qquad (5\text{-}6)$$

$$G=CV(S-S_0) \qquad (5\text{-}7)$$

Where S is the final substrate concentration (g/l); S_0 is the initial substrate concentration (g/l); k is the rate constant (d); t is the time (days); G is the cumulative gas production(l); V is the volume of reactor (l); C is the yield constant (l/g).

For a batch reactor the substrate remaining in the digester is given by integrating Equation (5-6)

$$S=S_0\exp(-k(t-t_0)); \; t>t_0 \qquad (5\text{-}8)$$

Where t_0 is the lag time (d).

This model (Fulford, 1988; McCarty and Mosey, 1991) describes the average reactor behavior at a longer retention time. From the Equations (5-8) and (5-7), the cumulativegas production can be predicted by

$G=CVS_0\,[1-\exp\{-k\,(t-t_0)\}]$ (5-9)

Rearranging by taking natural logarithm gives

$\ln(1-G/CVS_o) = -kt + kt_0$ (5-10)

The graphical analysis of the kinetic model for the data of the reactor R1, R2, R3 and R4 are shown in Figure 5.29 to 5.32. The rate constant and lag time were determined by using equation 5-10; ln (1-G/CVSₒ) versus time has been plotted for four different reactors.

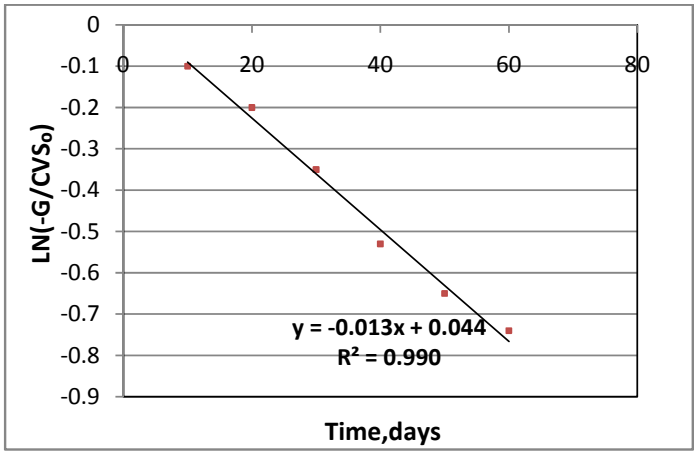

Figure 5.29: R1- Logarithmic plot of gas production with time

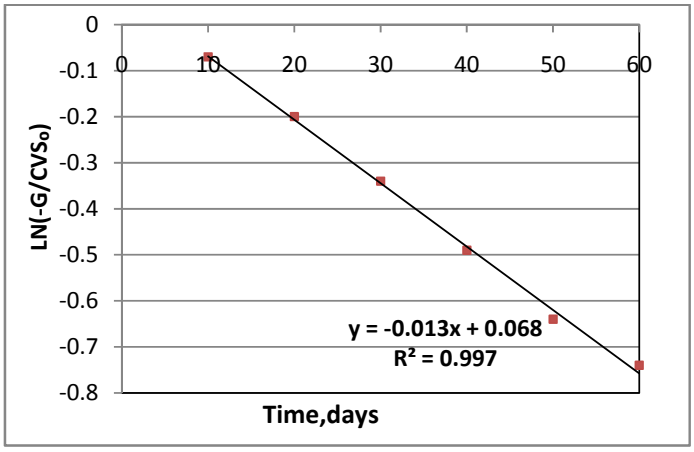

Figure 5.30:R2- Logarithmic plot of gas production with time

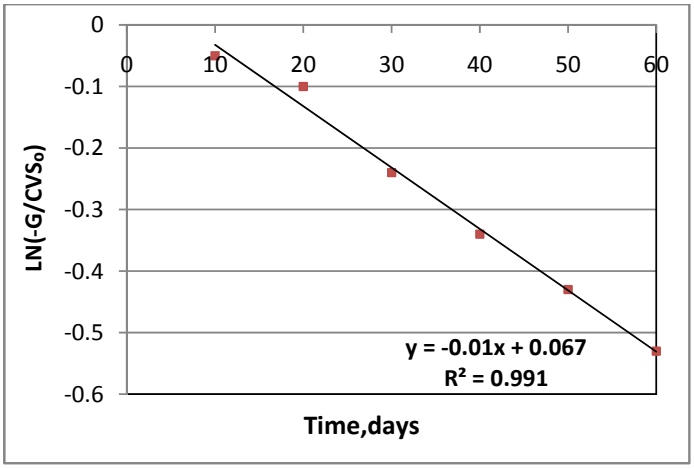

Figure 5.31:R3- Logarithmic plot of gas production with time

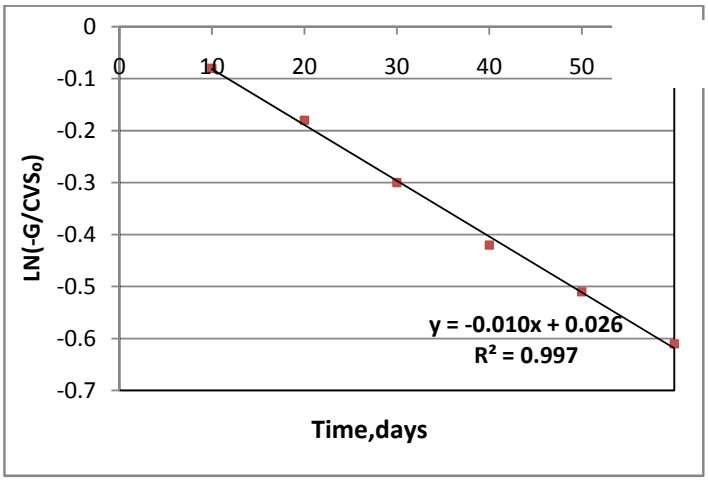

Figure 5.32:R4- Logarithmic plot of gas production with time

From the logarithmic plot of gas production with time in Figure 5.29 to 5.32 gives the rate constant, correlation coefficient and the predicted lag time. These values are presented in Table 5.3. To evaluate the accuracy of the model the observed lag time are also presented in the Table 5.3**.**

Table 5.3: Yield Constant, Rate constant, Correlation Coefficient, predicted and observed lag time for various reactors

Reactor	**Yield Constant(l/g)**	**Rate constant, k**	**Correlation Coefficient, R^2**	**Lag time,t_0 days(predicted)**	**Lag time,t_0 days(observed)**
R1	0.77	0.013	0.990	3.4	3
R2	0.91	0.013	0.997	5.2	3
R3	0.58	0.010	0.991	6.7	5
R4	0.63	0.010	0.997	2.6	4

From the kinetic model analysis for different reactors it can be concluded that knowing the yield constant (C), plot of ln (-G/ (CVS_0)) versus time gives slope of -kt and intercept of kt_0 from which the rate constant and lag time can be calculated.

The yield constant, rate constant and 'lag time' for various initial VS concentrations have been shown in Table 5.3. It was observed thatthe observed lag time was more or less in the same period as predicted by using equation (5-10). In all the reactors, logarithmic plot of gas production and time was linear with negative slope.The results fitted well in the first order kinetic model. Maximum yield constant was found for reactor R2 where, 75% fleshing and domestic sewage (1:1 ratio) were used with 25% cowdung on the total solids of the slurry.

5.13 Lag Time

The relation of refractory fractions of the feed mixture with observed lag time of different reactors is shown in Figure 5.33. It is found that larger the refractory fraction present in the feed mixture, longer the lag time for maximum gas generation. Besides this,cowdung on slurry have an effect on the startup of gas generation, which was also remarkable. As inoculum used for the reactors originated fromcowdung based biogas plant, the cowdung substrate got familiar environment on slurry and degraded easily than fleshing. For this reason in R3 reactor lag time was higher than other three reactors as there was no cowdung on the slurry.

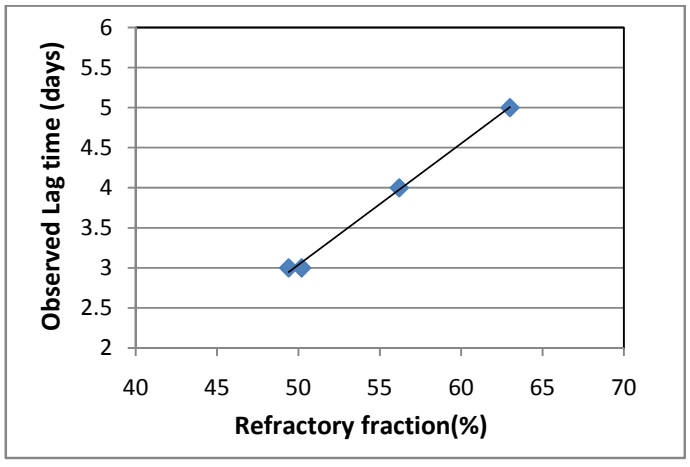

Figure 5.33: Relation between refractory fractions of feed mixture andobserved lag time of different reactors.

5.14 Economic Analysis

After analyzing all the data and from practical observation it was noticed that fleshing was suitable for gas generation and among the four test reactors the second reactor R2 was shown the best performance. Large amount of fleshing wastes is generated from leather industry every year. Fleshing based small scale biogas plant can be a good option for energy recovery, at the same time waste can be reduced. Consequently environmental hazards will be minimized to some extent. An economic analysis was done for investigating the viability of a fleshing based small scale biogas unit. As per UNIDO report in lean season 20.6 ton/day fleshing is generated from Hazaribagh tannery industry. If this amount is considered, 7519 ton waste is generated every year. From this study it was observed that 146.8 l/kg gas generates from fleshing (wet basis) that means each year **1,103,789.2** m^3 gas can be generated from this waste. If commercial rate (Tk. 30/m^3) of gas is considered, the amount of **Tk.33,113,676 (without considering the production cost)** per year earning can be possible from this huge amount of wastes.

Economic analysis of a fleshing based small scale biogas plant is described below:

Sl. No.	Description		Amount(Tk.)
1.	Capital Investment		
	a)Plant Construction Cost(100cft) According to IFRD,BCSIR		30,000
	b)Cost of cowdung with carrying charge 2.0 ton@ 2000Tk		4,000
		Total	**34,000**
2.	Yearly operating Cost		
	a) Raw material		
	i. Cost of Fleshing with carrying charge (20 kg*365 =7.3 ton ~ 7.5ton@ 650 Tk.)		4,875
	ii. Cost of cowdung with carrying charge 4.0 ton@ 2000Tk		8,000
	iii. Cost of domestic sewage only carrying charge 12 month@ 300Tk.		3,600
	b) Labour and maintenance		6,000
		Total	22,475
3.	Depreciation Cost		
	Plant construction cost @ 3%		900
		Total	**23,375**
4.	Yearly Income		
	a)Daily gas production		3.02 m^3
	b)Yearly gas production		1101 m^3
	c)Cost of total gas @Tk.30/m^3 (Commercial rate)		**33,030**
	d) Fertilizer (excluded)		-
		Total	**33,030**

Considering the life time of biogas plant is about 30-35 years and the bank interest is 12%; the following terms have been found out:

a) NPV(Net present value)

b) BCT(Benefit-Cost ratio)

c) PBP(Pay back period)

d) IRR(Internal Rate of Return)

e) NPV : NPV has been calculated from the given relation:

NPV=PVB-PVC, where, PVB=Present value of benefit

PVC=Present value of cost with above bank interest and 30 years plant life.

$$PVB = 33,030 \times [\{ (1.12)^{30} -1\}/ \{.12\times (1.12)^{30}\}] = 266,221.8$$

and $PVC = 23,375 \times [\{(1.12)^{30} -1\}/ \{.12\times (1.12)^{30}\}] +34,000 = 222,402.5$

a) NPV= PVB-PVC = 43,819.3

b) BCR = PVB/PVC = 1.20 (BCR>1)

c) Total fixed investment / Net income per year = 34,000/9,655= 3.52 ~ 3.5 years

d) IRR: The internal rate of return is the rate at which NPV=PVB-PVC = 0 that is PVB=PVC, Let the interest rate is r% and plant life is 30 years, Then-

$$33,030 \times [\{(1+r)^{30} -1\}/\{r\times (1+r)^{30}\}] = 222,402.5$$

Error and trial method r is found to be 14.7%.So, the IRR= 14.7%

Calculated Results

a. NPV (Net present value) = 43,819.3

b. BCR (Benefit –Cost ratio) = 1.20

c. PBP (Pay back period) = 3.5 years

d. IRR (Internal rate of return) = 14.7%

If NPV is positive, BCR is greater than 1 and IRR is greater than normal rate of interest, then the project is acceptable and viable. Without considering the fertilizer value, as no experiments have been conducted for the digested slurry, the economic analysis has shown positive results. Therefore, from the calculated results of economic analysis it can be concluded that the fleshing based biogas plant in pilot scale is economically and commercially sustainable.

5.14 Summary of the Findings

The summary of the findings from the analysis of the experimental data are given below:

- Fleshing used for test reactors contained 82.57% volatile solids. But the C/N value of the fleshing was 2.64, which was too low for anaerobic digestion. The C/N value of the slurry was increased by mixing fleshing with cowdung and domestic sewage and from the performance of the reactors it can be concluded that fleshing with cowdung and domestic sewage is highly potential substrate for gas generation by anaerobic digestion.

- Among the four test reactors, maximum gas was produced by R2 reactor on which 75% of the total solids (6% total solid) of the slurry were fleshing and domestic sewage. In all the reactors domestic sewage and fleshing were mixed in the ratio of 1:1. Reactor R3 (100% fleshing and sewage on 6% total solids of the slurry) was shown the lowest range of daily gas production.The trend of daily gas production profiles also indicated that cowdung has significant effect on gas production rate. A gradual shift was observed in the period of peak gas production with increasing VS concentration.The higher the initial volatile solid concentration, the more time was required for peak gas production of the reactor.

- Cumulative gas productions were observed 22,200ml, 24,960 ml, 12,145ml and 14,850 ml from test reactors R1 (VS concentration of 55.33 g/l), R2 (VS concentration of 52.45g/l), R3 (VS concentration of 50.80 g/l) and R4 (VS concentration of 51.56 g/l) respectively. A significant amount of gas was produced by all the four reactors. Even though R2 reactor contained less

amount of cowdung than R1 reactor, there also gas generation rate was higher. Fromthis it can be concluded that amended fleshings with domestic sewage when mixed with certain amount of cowdung then it becomes highly potential substrate for gas generation. Cowdung has significant effect on gas production but have to be used in certain proportion.

- The gas generation in all the four reactors almost ceased at the end of 60 days. So the digestion period was considered 60 days.

- During anaerobic digestion of solid waste, biogas generation is more specifically related to reduction of biodegradable fraction of VS in the digester. R2 and R3 reactors achieved around 52% VS reduction and more gas production also observed there, where as in reactors R3 and R4 (fleshing concentration was more in the slurry of this two reactor), VS reduction were 42% and 45% respectively. This indicates that VS reduction rate not only depends on initial concentration but also on types of volatile matter of the slurry. The results draw attention to that amended fleshing with sewage was not very much suitable for optimum gas generation but when it was mixed with cowdung by appropriate proportion, it presented the best performance.

- In the four reactors R1, R2, R3 and R4 specific gas production in terms volatile solid fed were 0.401, 0.476, 0.239 and 0.288 l/g respectively. The specific gas production obtained was comparable with the trends reported by Thangamani et al. (2009).

- It was noticed that when room temperature increased in the digestion period, the gas production was also increased. This confirmed the dependency of biogas generation on temperature. The entire test was conducted at a temperature 30°C ± 3 throughout the digestion period.

- Gas generation was observed in different test reactors at pH ranges of 6.8 to 7.15, 7to 7.2, 8.61 to7.3 and 7.49to 7.32 respectively.These ranges were in favorable range for anaerobic digestion .The highest gas production was for the pH ranges of 7 to 7.2 for R2 reactor. Initial pH for R3 reactor was quite high but that was buffered by the process itself.

- In reactor R1 48.02% COD reductionwas achievedby the process and for the R2, R3 and R4 reactors COD reduction rate were 50.67%, 44.80% and 44.61% respectively.

- Methane content of the biogas for all the test reactors were 72%, 73%, 70% and 72% by volume respectively, which were significant values to consider the biogas as clean fuel. Reactor R2 consist the highest methane yield which was remarkable.

- It is essential to monitor the biodegradable fraction of VS in the feed to have better operational control over the process. The biodegradability factor indicates the presence of resistant volatile matter (such as lignin) which is the major portion of volatile solids in the digester. A graphical model has presented which gave the amount of refractory fraction in VS in a digester. So the biodegradable fraction of the slurry of a digester can be determined by this model.

- Kinetic analysis of the data revealsthat first order kinetic model is adequate to describe the anaerobic co-digestion of animal tissue with other substrate. The lag time obtained from the kinetic model equation (5-10) for various initial VS concentrations were comparable with the experimentally observed time period. Theobserved lag times weremore or less in the same period as predicted by using equation (5-10).

- The observed lag time values for different reactors indicate that larger the refractory fraction present in the feed mixture, longer the lag time for maximum gas generation.

- Economic feasibility study of a pilot scale fleshing based biogas plant has been shown. All the computations of economic analysis have been shown favorable results. The payback period was found to be 3.5 years for this type of plant.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATION

6.1 CONCLUSIONS

The objectives of the study were to investigate the present solid waste management status of the Hazaribagh tannery estate and to provide a suitable management option for the tannery solid waste. The picture of the tannery estate was drawn by field survey and from critical observation; it was observed that improper or very often no management option is found for a large amount of tannery solid waste (fleshing), crude dumping of this waste is not only unaesthetical but also unsafe for the environment. The extensive laboratory examination showed that tannery waste fleshing contains significant quantity of volatile solids which is amenable for biodegradation. The aim of this study was to develop an appropriate technology for recovery of bioenergy from this portion of tannery solid waste. The studies were carried out in laboratory scale reactor for 60 days of digestion period. To determine the optimum condition for gas generation from tannery wastes, four different reactors with different proportion of substrate were used and a comparative study was carried out. The performance of anaerobic co-digestion of tannery solid waste has been evaluated in terms of VS destruction, biogas yield and methane content. Based on the study, the following conclusions can be drawn in support of biomethanation potential of the tannery solid waste fleshing:

- Amended fleshing with domestic sewage is highly potential substrate for biogas generation by anaerobic digestion when it is mixed with cowdung in appropriate proportion.

- The C/N value of the tannery solid waste fleshing is too lowwhich is unsuitable for anaerobic digestion. But without adding any chemicals the C/N value is increased by mixing fleshing with cowdung and domestic sewage and the high pH of the fleshing is also maintained by the process itself.

- The batch reactors were operated with initial volatile solid concentrations of 55.33, 52.45, 50.80 and 51.56 g/l and the corresponding specific gas

production obtained in terms of volatile solids fed was 0.401, 0.476, 0.239 and 0.288 l/g respectively. The VS destruction efficiency was 51.97%, 51.99%, 41.38% and 45.40% respectively. Even the reactor R3 which contains only fleshing and domestic sewage on the total solids of the slurry has been shown considerable results.

- Methane content in the biogas generated from different reactors varied from 70% to 73% by volume. COD reduction achieved in the test reactors 48.02% 50.67%, 44.80% and 44.61% respectively.

- Kinetic analysis of the data for different reactors reveals that first order kinetic model is adequate to describe the anaerobic co-digestion of fleshing with other substrate.

- Based on the volatile solids destruction efficiencies and specific gas production in terms of quantity of volatile solid fed, it is confirmed thatamended fleshingis amenable for anaerobic digestion for the recovery of energy with high methane content. For the optimum gas generation from fleshing all the criteria of R2 reactor can be adopted as it has been given the best performance.

- The optimum conditions for biogas generation from fleshing are: 6% total solid concentration, C/N ratio 17, pH 7.0 to 7.15 and temperature 30°C±3. Cowdung and domestic sewage will need to be used as co substrate. 25% of the total solids of the slurry will be cowdung and the remaining 75% will be fleshing and domestic sewage in the ratio of 1:1. Water need to be added to maintain the desired volume of the slurry.

- Based on the optimum condition (R2 reactor standards), the economic analysis of a pilot scale fleshing based biogas plant also shows favorable results. The payback period of this type of plant is found to be 3.5 years.

- Improper management of tannery waste already has done considerable harm to our environment. Therefore, it is high time to consider this issuegravely.

Energy is required in our everyday life as well as for the industry run. Hence,recovery of energy from the tannery solid waste by anaerobic digestion can be a sustainable and environment friendly option for tannery waste management.

6.2 Recommendation for further study

- Only one solid concentration was taken into account in this study, various solid concentrations can be studied.
- Only one percentage of inoculums was used in this research. Using various proportions of inoculums, reactors can be set up for finding optimum results.
- In this study slurry temperature was not monitored, in future research this can be monitored to analyze the temperature effect more specifically.
- Modification on digester arrangement should be done on future research work with inlet outlet arrangement, mixing arrangement, etc.
- Research can be done on design of biogas plant using different construction material for finding out optimum construction costing with good gas holding capacity.
- Since a huge amount of waste generates everyday from tannery industry, a central plant with special arrangement might be a permanent solution for this waste. For setting up a large scale biogas plant and to give complete solution more extensive research is needed.

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APPENDIX-A

Table A-1: Observed data (daily gas generation, ml)

Days	R1	R2	R3	R4
0	0	0	0	0
1	140	110	0	110
2	160	210	0	120
3	530	470	100	400
4	430	450	90	350
5	450	450	390	180
6	390	340	350	270
7	390	100	300	170
8	500	300	210	290
9	660	610	70	170
10	390	400	60	550
1st 10 days	4040	3440	1570	2610
11	440	450	60	220
12	280	390	60	300
13	770	900	100	220
14	250	820	70	170
15	220	500	50	180
16	280	550	110	170
17	390	*390*	180	570
18	440	220	110	330
19	390	390	280	410
20	390	440	270	280
2nd 10days	3850	5050	1290	2850
21	500	550	400	310
22	350	550	510	270
23	550	220	550	220
24	440	500	230	250
25	440	500	240	220
26	440	500	300	780
27	660	330	400	270
28	440	1100	350	250
29	330	550	220	2 50
30	550	550	280	220

Table A-1 (Continued)				
Days	**R1**	**R2**	**R3**	**R4**
3rd10days	4700	5350	3480	3040
31	440	610	220	240
32	440	440	240	250
33	440	220	230	230
34	1100	440	240	330
35	380	500	200	*300*
36	390	450	220	250
37	330	500	130	200
38	550	450	270	220
39	440	460	120	430
40	440	440	190	170
4th10days	4950	4510	2060	2620
41	440	500	110	170
42	330	550	220	110
43	440	500	120	250
44	490	610	255	170
45	220	550	90	350
46	170	500	150	170
47	220	390	300	170
48	170	280	180	170
49	170	280	250	170
50	170	170	280	200
5th10days	2820	4330	1955	1930
51	220	390	250	250
52	220	330	180	250
53	220	280	220	160
54	280	280	170	160
55	170	110	195	200
56	170	110	145	160
57	170	110	170	170
58	170	220	200	170
59	110	280	150	120
60	110	170	110	160
6th10days	1840	2280	1790	1800

Table A-2: Calculated Data (Cumulative Gas production, ml)

Days	R1	R2	R3	R4
0	0	0	0	0
1	140	110	0	110
2	300	320	0	230
3	830	790	100	630
4	1260	1240	190	980
5	1710	1690	580	1160
6	2100	2030	930	1430
7	2490	2130	1230	1600
8	2990	2430	1440	1890
9	3650	3040	1510	2060
10	4040	3440	1570	2610
11	4480	3890	1630	2830
12	4760	4280	1690	3130
13	5530	5180	1790	3350
14	5780	6000	1860	3520
15	6000	6500	1910	3700
16	6280	7050	2020	3870
17	6670	7440	2200	4440
18	7110	7660	2310	4770
19	7500	8050	2590	5180
20	7890	8490	2860	5460
21	8390	9040	3260	5770
22	8740	9590	3770	6040
23	9290	9810	4320	6260
24	9730	10130	4550	6510
25	10170	10810	4790	6730
26	10610	11310	5090	7510
27	11270	11640	5490	7780
28	11710	12740	5840	8030
29	12040	13290	6060	8280
30	12590	13840	6340	8500
31	13030	14450	6560	8740
32	13470	14890	6800	8990
33	13910	15110	7030	9220
34	15010	15550	7270	9550
35	15390	16050	7470	9850
36	15780	16500	7690	10100
37	16110	17000	7820	10300

Table A-2(Continued)				
Days	**R1**	**R2**	**R3**	**R4**
38	16660	17450	8090	10520
39	17100	17910	8210	10950
40	17540	18350	8400	11120
41	17980	18850	8510	11290
42	18310	19400	8730	11400
43	18750	19900	8850	11650
44	19240	20510	9105	11820
45	19460	21060	9195	12170
46	19630	21560	9345	12340
47	19850	21950	9645	12510
48	20020	22230	9825	12680
49	20190	22510	10075	12850
50	20360	22680	10355	13050
51	20580	23070	10605	13300
52	20800	23400	10785	13550
53	21020	23680	11005	13710
54	21300	23960	11175	13870
55	21470	24070	11370	14070
56	21640	24180	11515	14230
57	21810	24290	11685	14400
58	21980	24510	11885	14570
59	22090	24790	12035	14690
60	22200	24960	12145	14850

Table A-3: Temperature record

Day	Temp.(°C)	Day	Temp.(°C)	Day	Temp.(°C)
1	30	21	27	41	29
2	29	22	27	42	28
3	30	23	29	43	28
4	28	24	27	44	27
5	27	25	27	45	28
6	27	26	27	46	27
7	28	27	27	47	28
8	28	28	28	48	27
9	28	29	26	49	27
10	27	30	26	50	27
11	27	31	27	51	27
12	27	32	27	52	27
13	28	33	27	53	27
14	28	34	27	54	28
15	28	35	28	55	28
16	29	36	29	56	27
17	28	37	29	57	27
18	28	38	29	58	27
19	27.5	39	29	59	27.5
20	28	40	29	60	27

Table A-4: Characteristics of different Sample

	Fleshing			**Domestic Sewage**		
Parameters	F1	F2	F3	D1	D2	D3
pH	10.99	11.0	10.98	6.15	8.2	7.8
TS (%)	13.38	13.33	12.12	5.0	15	13
VS (%)	82.57	81.34	80.97	82.0	78.89	87.76
Oil (%)	9.50	6.96	7.53	2.32	2.1	.89
Protein (%)	44.16	46.78	48.94	25.32	22.45	14.67
Moisture content (%)	86.62	87.77	84.52	95	85	87
C/N Ratio	2.64	2.23	2.76	20	18	24
COD(mg/l)	Not Done			1329	703	876

Table A-5: Volatile solid conc. at different digestion time for different reactors

Time, days	R1	R2	R3	R4
0	55.33	52.45	50.8	51.56
10	50.098	48.67	48.08	47.44
20	45.92	43.53	45.853	42.93
30	39.03	38.81	40.13	38.89
40	32.616	32.27	37.59	33.99
50	29.01	28.22	32.88	30.94
60	26.57	25.18	29.78	28.15

Table A-6: COD values at different digestion time for different reactors

Time, days	**COD (g/l)**			
	R1	R2	R3	R4
0	78.6	59.2	61	46.58
10	71.7	56.76	56.78	41.93
20	65.19	49.08	52.48	38.76
30	56.45	43.7	46.89	34.68
40	46.56	36.87	43.03	29.42
50	42.11	32.98	37.69	30.87
60	40.86	29.2	33.67	25.8

Table A-7: pH of different reactors

Time, days	R1	R2	R3	R4
0	6.8	7	8.61	7.49
10	6.7	6.9	7	6.7
20	7.12	7.15	7.3	7.2
30	7.15	7.18	7.4	7.59
40	7.13	7.26	7.44	7.3
50	7.12	7.13	7.45	7.42
60	7.15	7.2	7.3	7.32

Table A-8: Refractory fraction, biodegradable fraction and total VS destruction observed in the reactors

Reactor	Refractory fraction of VS	Biodegradable fraction of VS	% VS destruction (observed)based on total VS
R1	0.494	0.506	52
R2	0.502	0.498	52
R3	0.630	0.370	41
R4	0.562	0.438	45

Table A-9: Composition of produced gas of different reactors

Digestion time(day)	R1		R2		R3		R4	
	CH_4 (%)	CO_2 (%)	CH_4 (%)	CO_2 (%)	CH_4 (%)	CO_2 (%)	CH_4 (%)	CO_2 (%)
0	0	0	0	0	0	0	0	0
7	48.5	51.5	47.4	52.6	46.5	53.5	46.4	53.6
14	67.8	32.2	68.9	31.1	65.6	34.4	67.7	32.3
21	69.5	30.5	70.6	29.4	67.4	32.6	68.2	31.8
28	70.2	29.8	71.8	28.2	68.6	31.4	70.3	29.7
35	71.1	28.9	71.9	28.1	69.7	30.3	70.6	29.4
42	71.7	28.3	72.4	27.6	69.9	30.1	71.2	28.8
56	72.1	27.9	72.6	27.4	70.4	29.6	71.6	28.4

Appendix-B

Figure B-1: Surrounding Area of Hazaribagh, Dhaka

Figure B-2: Dumped Waste at Roadside (Raw Trimming)

Figure B-3: Chrome Shaving Dust is Converted to Poultry Feed

Figure B-4: Pile of Raw Trimming at Open Space

Figure B-5: Preparing Glue from Raw Trimming

Figure B-6: Chrome Shaving Dust

Figure B-7: The Working Environment of Fleshing Processing Zone

Figure B-8: Labours are Working at Fleshing Processing Zone

Figure B-9: Fleshing Burning for Recovering Fat

Figure B-10: Recovered Fat from Fleshing

Figure B-11: Laboratory Set up of R3 reactor

Figure B-12: Produced Gas Burning (R1 Reactor)

Figure B-13: Produced Gas Burning (R3 Reactor)

Figure B-14: Gas Burning (R2 Reactor)

Figure B-15: Orsat Gas Analyzer