INVESTIGATION ON BIOGAS GENERATION AND PURIFICATION USING LIGNOCELLULOSIC BIOMASS AND CATTLE DUNG

A Thesis

Submitted in Partial Fulfillment of the Requirements for the Award of the Degree of

DOCTOR OF PHILOSOPHY

By

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Dedicated to my parents…

Mrs. Renuka Das

and

Mr. Kameswar Das

Whose endless faith and blessings always

inspired me to move forward

Declaration

I hereby certify that the information presented in this thesis is entirely my own research and contains as its main content work except where otherwise stated, which has not previously been submitted for a degree or diploma at this institute or any tertiary educational institution.

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Certificate

It is certified that the work contained in the thesis entitled "**Investigation on Biogas Generation and Purification using Lignocellulosic Biomass and Cattle Dung"** by **Manjula Das**, a student in the Department of Mechanical Engineering, Indian Institute of Technology Guwahati, India, for the award of the degree of **Doctor of Philosophy** has been carried out under my supervision and this work has not been submitted elsewhere for the degree.

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ABSTRACT

Depletion of fossil fuel and increase in environmental pollution at an alarming rate has motivated the researchers to look for the environmentally friendly as well as cost effective alternative sources of energy. On the other hand biogas production from biomass is getting a lot of attention due to its easy availability and relatively simple biomass to energy conversion technology. Co-digestion of biomass with cattle dung is another promising method of converting biomass to energy through anaerobic digestion.

In the most of the developing countries like India, China etc. the principal occupation of the people is crop production and the crop residues remained after harvesting is a major problem to deal with. These biomasses are lignocellulosic in nature as they contain cellulose, hemicellulose and lignin. They are not economically used rather disposed of in the open environment or burnt causing serious health problem and environmental pollution. In the present work, lignocellulosic biomasses are assessed for the use of anaerobic digestion with the objective of generating biogas from it and performing kinetic study on the produced biogas. Thus the aim of the present work is focussed to investigate the effectiveness and the performance characteristics of anaerobic digestion of lignocellulosic biomass for biogas production in batch mode.

The produced biogas mainly contains methane and carbon dioxide. On the other hand carbon dioxide is a non-combustible constituent of biogas which in fact lowers the heating value of biogas and increases compression and transportation costs [Mittal, 2006]. So to improve the effectiveness of biogas as fuel, carbon dioxide has to be removed from it. Therefore present study is also proposed towards the process development to obtain enriched methane from biogas.

To assess the potentiality towards biogas production, fifteen different types of biomasses are collected and characterized. Based on the results obtained from the characterization, five different lignocellulosic biomasses viz. bamboo dust, saw dust, sugarcane bagasse, rice straw and rice husk are selected upon which small scale anaerobic digestion are performed. These biomasses are having high volatile matter content (above 60%) and high fixed carbon content (above 10%) which make them potent for biogas production.

Parametric study of biogas production from lignocellulosic biomass by anaerobic digestion process in batch mode is performed on all the five biomasses separately mixed with cattle

dung. Effect of total solid and particle size of biomass on biogas production is studied and found that with 8-9% of total solid and 0.355 mm of particle size maximum amount of biogas can be produced. Effect of temperature on biogas production from lignocellulosic biomass is also studied at five different temperatures from 35°C to 55°C at a step of 5°C and found that with increase in temperature of the digestate from 40°C to 55°C, biogas production from substrates can be increased. It is also observed that in mesophilic condition, biogas generation is the highest at 35°C followed by 40°C. Study on the effect of agitation and addition of biochar to feedstock is also carried out. With agitation biogas production from the substrate is found to be improved as compared to the non-agitated substrate. The biogas production is also optimized with addition of 5% biochar in the substrate. Out of these five biomasses bamboo dust, saw dust and sugarcane bagasse has shown very good results as compared to rice husk and rice straw.

The kinetics of biogas production is studied by applying first order kinetic model and modified Gompertz model to biogas production from biomass mixed with cattle dung. Due to certain limitation of the first order kinetic model modified Gompertz model is proposed for the kinetic study. Modified Gompertz plot has shown very good correlation (R^2=0.99) for simulating cumulative biogas production but it cannot predict the effect of temperature on biogas production. Hence, this model is reformed using the relationship between the kinetic parameters of the model with temperature. This renewed model is able to predict the effect of temperature on biogas production from biomass mixed with cattle dung within the range 40°C-55°C temperature.

Methane enrichment study is carried out on biogas by chemical absorption method using sodalime in fixed bed which is found to be quite effective than the other available methods.

Keyword: Lignocellulosic biomass, biogas, characterization, co-digestion, biomethanation, agitation, parametric study, kinetic study, kinetic model, methane enrichment.

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Date:

Contents

Nomenclature

r_v	Volumetric methane production rate, LCH_4/L fermentor /day
S_0	Influent total volatile solids (VS) concentration, g/L
B_0	Ultimate methane yield, LCH_4/g.VS added as $\theta \rightarrow \infty$
k	Kinetic parameter
G	Methane output from the fermentor (dm^3/day)
V	Volume of the fermentor (m^3)
Y_v	the methane output per unit of fermentor volume per day
Q	Degree of degradation of the organic matter (%)
k_s	Monod kinetic constant
μ	Specific growth rate of microorganisms
μ_{max}	Maximum specific growth rate of microorganisms
p	Population density
S	Substrate Concentration
P	Cumulative specific biogas production in ml/g VS
A	Biogas production potential in ml;
U	Maximum biogas production rate in ml/g VS/day
R_c	Refractory coefficient (non-biodegradable VS/total VS)
B	Volumetric methane yield (l CH_4/g VS added) after limited time
f	Pre exponential factor
T	Temperature
R	Universal gas constant
E_a	Activation energy
y	Gas production rate at any HRT
θ	Hydraulic retention time, day
λ	Lag phase period (i.e. minimum time to produce biogas) in day

Subscript

max	Maximum

Abbreviation

OLR	Organic loading rate in kg VS day^{-1} m^{-3}
LR	Loading rate in kg VS day^{-1}
TS	Total solid (%)
HRT	Hydraulic retention time (days)

Abbreviations

HRT	:	Hydraulic retention time	EDX	:	Energy dispersive x-ray
CSTR	:	Completely stirred tank reactors	SEM	:	Scanning electron microscope
VS	:	Volatile solid	SI	:	Spark ignition
SSD	:	Solid state digester	CI	:	Compression ignition
PSA	:	Pressure swing adsorption	LHV	:	Lower heating value
TSA	:	Temperature swing adsorption	M	:	Moisture
GC	:	Gas chromatograph	O	:	Oxygen
CNG	:	Compressed natural gas	H	:	Hydrogen
VM	:	Volatile matter	Si	:	Silicon
FC	:	Fixed carbon	CV	:	Calorific value
COD	:	Chemical oxygen demand	IS	:	Indian standard
C	:	Carbon	BD	:	Bamboo dust
N	:	Nitrogen	SB	:	Sugarcane bagasse
LR	:	Loading rate	RH	:	Rice husk
TS	:	Total solid	SD	:	Saw dust
TERI	:	Tata Energy Research Institute	RS	:	Rice straw
OLR	:	Organic loading rate	CD	:	Cattle dung
CHP	:	Combined heat and power	MEA	:	Mono-ethanolamine
MPa	:	Mega pascal	ASTM	:	American Society for Testing and Materials
KVIC	:	Khadi and Village Industries Commission	APHA	:	American Public Health Association

List of Figures

List of Tables

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Depletion of fossil fuel and increase in environmental pollution at alarming rate has motivated the researchers to look for environment friendly as well as cost effective sources of energy. Thus, various forms of renewable energy, such as, solar, wind, tidal, hydel, wave and biomass are getting attention worldwide during last few decades. Solar photovoltaic systems are limited due to high cost of production while use of wind, tidal, hydel and wave energy is site specific. Harnessing energy from biomass is gaining popularity in developing countries due to the high availability of biomass and bio-waste. One of the options to convert biomass to energy is the production of biogas through anaerobic digestion. The advantage of biogas technology is ease in production and sustainability. The estimated annual biomass production in India itself is 200 million tons, which is distributed almost evenly in the country [Singh, 2007]. This is equivalent of 20 GW of installed capacity. In addition, agro-residues and woody bio-residues from wastelands (estimated at 60 million hectares) could add another 100–300 million tons, which amount to 45 GW of installed capacity [Singh, 2007; MNRE report, 2005]. These abundantly available biomass resources are potential candidate for generation of biogas. However, technology related to production of biogas from lignocellulosic biomass is at its infant stage demanding for a thorough research in the line. Co-digestion of biomass with cattle dung is another promising method to convert biomass to energy through anaerobic digestion so as to reduce the emission of oxides of carbon and nitrogen significantly.

1.2 MOTIVATION

Biomass can be utilized for energy production by either gasification or by digestion processes. For gasification the substrate is needed to be dry and moisture free but when substrate is heavily loaded with moisture, digestion of the substrate for energy production is the only option. Digestion of biomass can be either aerobic or anaerobic. But energy production cannot be obtained using aerobic digestion as it does not produce any combustible item. On the other hand anaerobic digestion of biomass produces biogas which is an immense source of energy. Hence the author is motivated to adopt the anaerobic digestion process to check the potentiality of lignocellulosic biomass.

In some of the countries like India, Nepal, Bangladesh, China etc. biogas production from cattle dung by anaerobic digestion is getting importance due to increasing cost of petrol and diesel as this technology can reduce environmental pollution and generate a relatively cheap and readily available source of energy in dairy farm. Moreover it is an effective way of managing cattle dung and at the same time producing an eco-friendly fertilizer for use in agricultural purpose. There are about 5,000,000 household in rural areas of China using anaerobic digesters [Henderson and Eng., 2009] to process rural organic wastes.

The principal occupation of the people in the most of the developing countries is crop cultivation. Crop residues remained after harvesting is therefore a major problem to deal with. Some parts of these crop residues are used as a fuel or feed for the domestic applications. Further biomass is burnt to produce smoke for driving out flies and mosquitos causing air pollution. Lignocellulosic biomass such as bamboo dust, sugarcane bagasse, saw dust, news paper, etc. are also available in plenty in these countries. These bio-wastes are either uneconomically used or disposed of into landfills without treatment causing serious pollution problems. Inappropriate disposal methods can cause adverse environmental and health related problems like pathogen contamination, odour, air borne ammonia, greenhouse gases etc. [Harikishan, 2003]. It is observed that the major part of these residues is thrown away in open environment. These heaps of bio-wastes become major hub of mosquitos, ants, rats etc. which eventually cause disease to people like chikungunya, plague, dengue, etc. The mosquito-borne viral disease chikungunya, erupted in Kerala towards May-end in the year 2007, claiming 40 lives while 7,000 people were admitted in hospitals in the South and Central districts of Kollam, Pathanamthitta, Kottayam and parts of the capital city [http://iictenvis.nic.in/Database/Chikungunya_outbreak_in_Kerala_2007_1057.aspx; 26/9/2014]. The outbreak of plague in September 1994 was also an outcome of the great piles of rubbish which remained uncollected in the surat city, Gujrat offering an ideal habitat for rats [World Resources, 1996-97].

These lignocellulosic biomasses are considered to be a potential source of energy due to its moderate calorific value, high volatile matter and cellulose content. But these biomasses are difficult to degrade in anaerobic condition due to the presence of lignin. So, looking into the potentiality of lignocellulosic biomasses, study on harnessing biogas is needed. Since biogas production from lignocellulosic biomass is still in research level, so a proper research methodology is needed to be investigated. Kinetic study on biogas production is also

important for correct understanding of the chemical reactions going on during anaerobic digestion of lignocellulosic biomass.

Further, removal of carbon di-oxide from the biogas produced by anaerobic digestion is important in terms of reduction of atmospheric pollution. Also, to enhance the calorific value of biogas removal of carbon di-oxide present in it is necessary. Thus there is a requirement of an appropriate technology for simple purification process to separate carbon dioxide from methane in biogas.

1.3 COMPOSITION AND PROPERTIES OF BIOGAS

The main constituents of biogas are methane and carbon dioxide. Apart from that, a trace amount of hydrogen sulphide, nitrogen, and hydrogen are there depending upon the various substrates used for producing the biogas. Table 1.1 shows the typical composition of biogas.

Table 1.1 Typical composition of biogas

[Deublein and Steinhauser, 2008]

Compound	Chemical Composition	(%)
Methane	CH_4	55-70
Carbon dioxide	CO_2	44-28
Hydrogen sulphide	H_2S	1-2
Other gases	---	

Biogas is non-poisonous in nature, has no offensive smell and it burns with a clean blue soot less flame. Typical properties of biogas are given in Table 1.2.

Table 1.2 Typical properties of biogas

[Deublein and Steinhauser, 2008]

Properties	Values
Critical pressure	75-89 bar
Critical temperature	-82.5 $^{\circ}$C
Calorific value with CO_2	18.7 MJ/ m^3
Calorific value without CO_2	26 MJ/ m^3
Density	1.0994 kg/m^3
Specific gravity	0.94
Viscosity	1.297x 10^{-5} kg/sec/m
Ignition temperature	700 $^{\circ}$C
Energy content	6.0-6.5 $kWhm^{-3}$

1.4 APPLICATIONS OF BIOGAS

Major constituent of biogas are methane and carbon dioxide. Methane is the prime constituent of natural gas. So, if somehow carbon dioxide can be removed from the biogas, it will be a source of immense energy which can be used effectively for different purposes like cooking, lighting, vehicle fuel, generation of electricity. After scrubbing the biogas it can be compressed and used as vehicle fuel like CNG and also it can be stored in cylinders and transported to other places.

1.5 ANAEROBIC DIGESTION PROCESS

Biogas can be produced by the fermentation or anaerobic digestion of organic matter e.g. biomass, manure, crop residues, municipal waste, industrial waste etc. Anaerobic digestion is a process in which microorganisms degrade the biodegradable part of the organic material in the absence of oxygen to produce biogas mainly consists of methane and carbon dioxide. The digestion process takes place through various reactions and interactions among the methanogens and substrates fed into the digester as input [Mahanta et al., 2006]. The whole digestion process is divided into four main steps to understand the process properly. They are known as

- Hydrolysis of organic matter to soluble compounds
- Acidogenesis of soluble compounds fermenting to volatile fatty acids
- Acetogenesis forming hydrogen, carbon dioxide and acetate
- Methanogenesis producing biogas

As shown in Fig. 1.1, the digestion process starts with hydrolysis of the substrates given as input and breaks them down to insoluble carbohydrates, which now become available for other bacteria. After that the Acidogenic bacteria convert the sugars and amino acids to carbon dioxide, hydrogen, ammonia and organic acid. Then the acetogenic bacteria convert these organic acids into acetic acid along with additional ammonia, hydrogen, and carbon dioxide. Finally, methanogens convert these products to methane and carbon dioxide. Anaerobic fermentation produces biogas on renewable basis, eliminates foul smell and reduces harmful bacteria of organic wastes, improves nitrogen and phosphate content of resulting sludge to yield highly enriched fertilizer [Mittal, 1996]. The reaction that takes place in the process of methane formation is expressed by the Eq. 1.1-1.3 [Mata-alvarez et al., 2000].

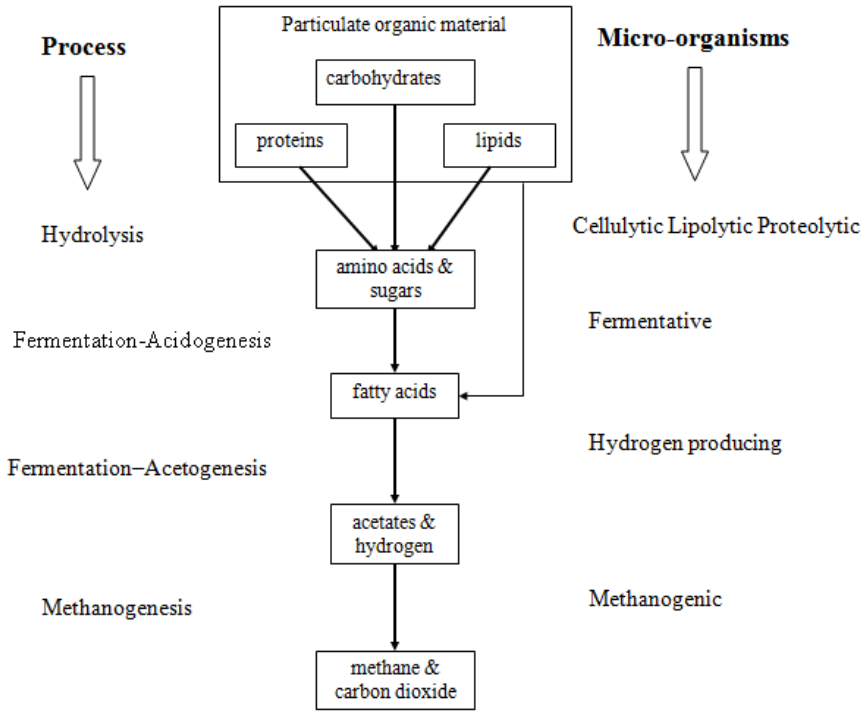


Fig. 1.1 Stages of an anaerobic digestion [Mata-alvarez et al., 2000]

$$\underset{\text{acetic acid}}{CH_3COOH} \rightleftharpoons \underset{\text{methane}}{CH_4 + CO_2} \quad (1.1)$$

$$2CH_3CH_2OH + CO_2 \rightleftharpoons CH_4 + 2CH_3COOH \quad (1.2)$$

ethanol

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad (1.3)$$

1.6 TYPES OF BIOMETHANATION PROCESS

Anaerobic digestion can be performed as a batch process or a continuous process. In a batch system biomass is added to the reactor at the start of the process. The reactor is then sealed for the duration of the process. Since the batch digestion is simple and requires less equipment and lower levels of design work, it is typically a cheaper form of digestion as compared to the continuous type digesters. In continuous digestion processes, organic matter is added and the end products are removed in a continuous manner thus resulting in constant production of biogas.

1.7 COMMONLY USED FEED MATERIALS FOR BIOGAS PRODUCTION

Biogas production from all feed material is not the same. It varies from substrate to substrate. Apart from that many other factors are there which affect the production of biogas. Some of them are C:N of substrate used, temperature, pH value of the slurry, loading rate of input, hydraulic retention time, toxicity of slurry, dilution and consistency of input etc. Effect of agitation and additives on biogas production is also quite significant.

Different kind of material used as feed for bio-methanation can be classified as animal waste, plant waste and domestic waste. Some of them are categorized in Table 1.3.

Table 1.3 Various kind of feed material used for bio-methanation processes

Animal Wastes [Budiyono et al., 2010; Trujillo et al., 1991; Yusuf et al., 2011; Patil et al., 2011; Wong and Cheung, 1989]	**Plant wastes** [Mähnert et al., 2005; Das Ghatak and Mahanta, 2014]	**Domestic waste** [Viswanath et al., 1992; Knol et al., 1978]
Cattle dung	Grass clipping	Raw garbage
Rabbit wastes	Bean stalks	Bread
Horse manure	Bagasse	Potato tops
Pig manure	Cut Straw	Paper
Poultry manure	Peanut stalk and leaves	Kitchen vegetable scraps
Night soil	Wheat straw	Cabbage
Human urine	Rice straw	Tomato
Mixed slaughter house waste	Corn stalks	Fruit and vegetable waste

1.8 PRETREATMENT OF BIOMASS

Lignocellulosic biomasses are rich in three different types of polymer like cellulose, hemicellulose and lignin [Raven, 1992]. The cellulose maintains the crystalline fibrous structure as the core of the complex. Hemicellulose is located between the micro- and macrofibrils of cellulose. Lignin is responsible for the structural role of the matrix in which the cellulose and hemicellulose is bounded [Faulon, 1994]. Approximately 44% of the fermentable materials are shielded by lignin [Robbins, 1979]. Due to poor degradation of lignin in anaerobic condition, the rate and extent of digestion of lignocellulosic material becomes incomplete [Fan, 1988]. So, to reduce the digestion period of the biomass

pretreatment is done. Pretreatment is a process that alters the cellulose structure of the biomass rendering fast hydrolysis of both the cellulose and hemicellulose producing biogas in short span of time. In this process the lignin content of the biomass is first broken down by various means like mechanical/physical, chemical, biological etc. and then utilised for biogas production. The most significant physical pretreatment include the particle size reduction [Fan et al., 1988], which eventually leads to the increase in available surface area and the release of intracellular components [Palmowski and Müller, 1999; Lehtomaki et al., 2006]. Mechanical pretreatment includes milling which helps in particle size reduction of biomasses.

1.9 PURIFICATION OF BIOGAS

Being non-combustible constituent of biogas, carbon dioxide does not contribute to the combustion of biogas; in fact it lowers the heating value of biogas and increases compression and transportation costs [Mittal, 2006]. Also, hydrogen sulphide present in biogas is very corrosive in nature which corrodes metallic parts including gas pipeline. This leads to the need for purification of biogas. Purified biogas can be compressed and used in I. C. engine. Compressed biogas can be stored in gas cylinder and transported wherever it is required. Purified gas provides reduction in green house gas emissions. Calorific value of biogas increases with purification. That is why purification is very necessary to use the biogas properly.

1.10 OBJECTIVES OF THE PRESENT WORK

The aim of the present work is to assess the potentiality of biogas production and removal of carbon di-oxide from it using locally available lignocellulosic biomass as feed material.
Following are the scope of the work:

1. Characterization of different types of biomass, e.g. rice straw, rice husk, saw dust, news paper, tea-waste, sugarcane bagasse, bamboo dust, gulmohar leaves, green banana leaves, dry banana tree, banana peel, banana pulp, dry tree leaves, elephant grass, switch grass and fresh cattle dung to identify the potential feed materials for production of biogas
2. Study on effect of various parameters such as particle size of biomass, pre-treatment of biomass, total solid of substrate, temperature of substrate, addition of biochar on biogas production from selected lignocellulosic biomass
3. Kinetic study of the biogas production rate by anaerobic digestion process and improvement of a kinetic model for both the mesophilic and thermophilic range
4. Carbon dioxide removal in a fixed bed to improve the quality of biogas

1.11 ORGANIZATION OF THESIS

This thesis comprises of seven Chapters. Chapter 1 discusses the energy scenario of developing countries like India, China etc., fundamentals of anaerobic digestion process, motivation and objectives of the present work. Chapter 2, reports the detailed review of literature on the various methods to improve biogas production, use of different feed material for biogas production and different aspects of kinetic modelling study, etc. for batch digestion. Characterization of biomass is discussed in chapter 3. Description of experimental set-ups, experimental procedure and results and discussions of parametric study of biogas production from lignocellulosic biomass by anaerobic digestion processes are presented in the chapter 4. In Chapter 5, kinetic study of biomethanation processes under batch mode and formulation of new kinetic model is discussed. Results of the kinetic study and modelling are presented and discussed in the same chapter. Design and development of carbon dioxide scrubber and the results of the biogas purification using sodalime are discussed in the Chapter 6. Chapter 7 summarizes the research findings and discusses scope for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Present chapter deals with the literature review on various aspects of production and purification of biogas. Sections 2.2 -2.8 include the effect of various parameters on biogas production, kinetic study of anaerobic digestion processes, biogas production in mesophilic as well as in thermophilic condition, carbon dioxide removal from biogas, etc. Summary of the literature review and the scope of the present research are presented at the end of the chapter under section 2.9.

2.2 FACTORS AFFECTING BIO-METHANATION PROCESSES

2.2.1 EFFECT OF TEMPERATURE ON BIOGAS PRODUCTION

Effectiveness of anaerobic digestion depends upon the intensity of bacterial activity. Thus it is essential to control the factors responsible for the same [Mittal, 1996]. Temperature is identified to be one of the important factors for efficient anaerobic digestion of biomass. Bushwell and Hatfield, 1996 identified the anaerobic bacteria and the conditions that promote methane production in the 1930s [Mahanta et al., 2004].

Lusk, 1998 studied different types of digesters with internal heating and found that gas production was the maximum in mesophilic condition (30°C-45°C). However, thermophilic condition (45°C-60°C) enhances the metabolic rates and specific growth rate of bacteria as compared to mesophilic condition [Lier, 1995]. Similarly Mackie and Bryant, 1995 claimed in four fold increase in biogas production with cattle dung as compared to that of in mesophilic condition.

Thermophilic stabilization of biogas digesters at 55°C temperature is truly economical as it produces more quantity of biogas [Vindis et al., 2009]. But anaerobic digestion in mesophilic condition is more common as compared to that in thermophilic condition due to the reduction in process stability, dewatering properties and requirements of large amount of energy for heating the substrate inside the digester. Vindis et al., 2009 identified the methane forming micro-

organisms and reported that methanogenic bacteria are distinct and different at both in mesophilic and thermophilic temperature regime.

Garba, 1996 investigated the effect of temperature on biogas production from lignocellulosic material and found that biogas production was the maximum at thermophilic temperature. Hashimoto et al., 1981 and Hills and Roberts, 1981 reported about higher digestion rate, improved solid setting and higher destruction of pathogen in the thermophilic temperature. Liar, 1995 observed that temperature acts as an accelerator for the anaerobic processes and determines whether a reaction can be performed by specific bacteria or not.

Varel et al., 1976 experimented on thermophilic methane production from cattle waste and found that the methane production was the maximum at 60°C. The process was initiated with ease and reported to be fast. The experimental observations indicate that methanogenesis was rapid with higher loading rate and shorter retention time.

Vindis et al., 2009 investigated both the thermophilic and mesophilic anaerobic digestion of three different types of maize varieties for biogas production and its quality in both approaches and found that methane content of biogas obtained from thermophilic digestion was higher than that of the mesophilic digestion by 2%. They reported that the thermophilic anaerobic digestion was 8 times faster than mesophilic degradation.

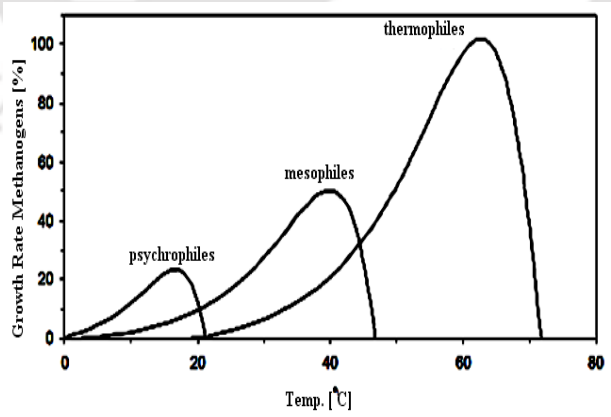


Fig. 2.1 Growth rate of methanogens under psychrophilic, mesophilic and thermophilic conditions [Liar e tal., 1997]

Lier et al., 1997 compared the growth rate of methanogenic bacteria in thermophilic, mesophilic and psychrophilic conditions as shown in Fig. 2.1. It is observed from the Fig. 2.1 that the growth rate of methanogenic bacteria is highest under thermophilic condition followed by mesophilic and psychrophilic conditions, respectively.

Sambo et al., 1995 studied the effect of temperature on biogas production and found that gas production was the highest at 50°C followed by 60°C and 40°C, respectively. Mahanta et al., 2004 experimented on the effect of temperature variation on anaerobic digestion of cattle wastes and found that biogas production was highest at 35°C followed by 45°C, 40°C and 30°C, respectively. Larsen et al., 1994 reported that digestion under thermophilic conditions has higher destruction rate of both pathogens and weeds compared to psychrophilic and mesophilic conditions.

Hashimoto et al., 1980 and 1981 and Chen et al., 1980 found that temperature affects the rate at which methane is produced but does not increase the amount of methane that can be produced from a unit mass of substrate. Therefore, they concluded that this fact is applicable to all other livestock manures and other high cellulosic materials too.

2.2.2 EFFECT OF FEED MATERIAL ON BIOGAS PRODUCTION

Different feed materials have different volatile matter content, fixed carbon content, cellulose content or different C:N ratio due to which biogas yield differs significantly with feed material. Busch et al., 2009, Kalra and Panwar, 1986, Somayaji and Khanna, 1994 have used crop residues like maize, grass, sugar cane, husk and straw, rice and wheat straw for production of biogas. It was found that biogas obtained from maize, grass and sugarcane has high methane (>72%) and low H_2S concentration (<100 ppm). It was also reported that the biogas production with straw is 456% more than that with the husk alone and 167% more than the mixture of straw and husk. The husk has very small gas potential.

PremaViswanath et al., 1992, Bardiya et al., 1996, Kalia et al., 1992 studied the effect of different fruit and vegetables as feed material on biogas production at different HRT and found that with these kind of feedstock higher rate of gas production rate even at low retention time. Mähnert et al., 2005 investigated three fresh and ensiled grass species in lab-scale batch

experiments at 35°C and reported production of good amount of biogas. Methane content in the produced biogas was found to be in the range of 50-58%.

Chua et al., 2008 constructed a small reactor to study the anaerobic digestion of food waste and found that the production of biogas ranged from 0.55 to 1.29 ml biogas/kg food waste. The addition of grease retarded the anaerobic process and addition of chicken manure increased the production rate. Table 2.1 presents the major findings of some of the authors on biogas yield with feed materials.

Table 2.1 Literature on various feed material and their results

Authors	Feed Materials used	Results
Busch et al., 2009	maize, grass, sugar cane	The process was extremely stable and no malfunction had been detected so far. The biogas obtained has high methane (>72%) and low H_2S concentration (<100 ppm).
Kalra and Panwar, 1986	husk and straw	The straw alone produced 456% more gas than the husk alone and 167% more than the mixture. The husk has very small gas potential.
Mähnert et al., 2005	fresh and ensiled grass species	biogas was in the range of 0.65-0.86 m^3/kg VS

2.2.3 EFFECT OF CO-DIGESTION OF BIOMASS ON BIOGAS PRODUCTION

Various researchers have worked on co-digestion of biomass with cattle dung as well as with other type of feed materials [Li et al., 2010; Hills and Roberts, 1981]. Jingqing et al., 2013 reported that when kitchen waste: pig manure: rice straw was in proportion of 0.4: 1.6:1, biogas production was found to be the highest. Somayaji and Khanna, 1994 worked on rice and wheat straw separately mixed with cattle dung in different proportion and found that biogas production was the maximum when rice straw was 100% and wheat straw was 40% with cattle dung as substrate. Similarly Kalia and Kanwar, 1990 worked on mixtures of fresh and partially-decomposed Ageratum and found that partially decomposed Ageratum and cattle dung in 3:2 ratio yielded about 9% more biogas than that of pure cattle dung. It is observed that when biomass is co-digested with other feed material in appropriate proportion biogas production can

be improved significantly. Table 2.2 presents some of the works on co-digestion of biomass with other feed material in batch mode obtained from literature.

Table 2.2 Literature on effect of co-digestion of biomass on biogas production

Author	Feed Materials used	Results
Hills and Roberts, 1981	fresh dairy manure and chopped field crop residues	The methane production per unit COD from fresh dairy manure was enhanced by addition of chopped field crop residues, upto a limit of non-lignin carbon to nitrogen ratio of 30:1.
Li et al., 2010	food waste with dairy manure	The gas production rate was enhanced by 0.8-5.5 times as compared to the digestion with dairy manure alone.
Jingqing et al., 2013	Rice straw with kitchen waste and pig manure	When kitchen waste: pig manure: rice straw was 0.4: 1.6:1, biogas production was the highest
Somayaji and Khanna, 1994	Rice and wheat straw in cattle dung	Maximum gas production at 100% rice straw and 40% wheat straw substitution in cattle dung
Kalia and Kanwar, 1990	Mixtures of fresh and partially-decomposed Ageratum	Fresh ageratum mixed with cattle dung in a ratio of 3:2 did not produce any gas but similar mixtures of partially decomposed Ageratum and cattle dung yielded about 9% more biogas than that of pure cattle dung.

2.2.4 EFFECT OF CARBON AND NITROGEN RATIO ON BIOGAS YIELD

Carbon is the major chemical element in organic wastes digested by bacteria to release methane and carbon-dioxide in the process. Microorganisms also require certain amount of nitrogen in feed to perform their function [Mittal, 1996]. The fermentative bacteria uses carbon 25 to 30 times as fast as nitrogen, thus necessitating the optimum C:N of 25 to 30:1. Deviation from this ratio slows down the process [Nijaguna, 2002]. A high C:N means that the nitrogen will be exhausted before carbon is digested and conversely, a low C:N ratio means too much nitrogen in relation to carbon, which results in high ammonium concentrations tending to become toxic to

anaerobic bacteria [Mittal, 1996]. Therefore an optimum mix of the input material is necessary to get the optimum C:N of 25:1 to 30:1.

Hills and Roberts, 1981 reported that the performance of digesters is the maximum when the C:N ratio of the feed material was between 25:1 to 30:1. Table 2.3 shows the C:N present in various feed material.

Table 2.3 C:N ratios in various organic wastes [Nijaguna, 2002]

Animal Wastes	**C:N**	**Plant wastes**	**C:N**	**Domestic waste and refuse**	**C:N**
Cow-dung	25:1	Grass clipping	19:1	Raw garbage	25:1
Sheep manure	20.1:1	Hay	18:1	Bread	20:1
Horse manure/mule	25:1	Corn stalks	60:1	Potato tops	25:1
Pig manure	14.4:1	Cut straw	48:1	Kitchen vegetable scraps	16:1
Poultry manure/pigeon waste	5.2:1	Sea weeds	19:1	Rags	12:1
Night soil	8:1	Peanut stalk and leaves	19:1	Household dirt	41:1
Farmyard manure(average)	14:1	Rice straw	67:1	Cabbage	12:1
Human urine	0.8:1	Bean stalks	32:1	Tomato	128:1

2.2.5 EFFECT OF LOADING RATE (LR) ON BIOGAS PRODUCTION

The rate at which biomass is supplied to the digester is referred to as loading rate (LR) and is expressed in terms of kg of volatile solids per $m^3$of digester capacity per day. The production of gas is dependent on LR. The size of the digester also consequently depends on the loading, which in turn depends on dilution, retention time and temperature of digestion. Different loading rate can be obtained by either changing the concentration of the solids in the influent or by varying the flow through the digester.

The total solids concentration (TS), loading rate (LR) and HRT are related by the following equation [Nijaguna, 2002]

$$LR = k\left(\frac{TS}{HRT}\right) \tag{2.1}$$

where

LR is kg VS day^{-1} m^{-3},

TS in %,

HRT in days

k is the percentage(%) of digestion.

According to Mohanrao, 1975 loading rates of plants based on night soil should be 1.04 to 2.23 kg VS per m^3 of digester capacity. He recommended higher loading rate for high ambient temperatures. Gore et al., 1981 studied the effects of variation of loading rate on biogas production and found that 100 kg of alternate day loading produced higher biogas as compared to 50 kg of daily loading. They also concluded that for a particular size of plant, an optimum value of loading rate will produce maximum gas and beyond that change in loading rate will not increase the gas production proportionately.

2.2.6 ROLE OF pH ON BIOGAS PRODUCTION

pH is the measure of acidity or alkalinity of a solution. During anaerobic fermentation, microorganisms require a neutral or mildly alkaline environment for efficient gas production. A pH between 7 and 8.5 is optimum range for increased gas yield [Mittal, 1996].

pH is a very important variable in anaerobic digestion. The pH value has a strong impact on degradation process. It affects the growth rate of acetogen and methanogen microorganisms. Ammonia inhibition phenomena depend on pH and increases with increase in it [Campos and Flotats, 2003].

Fig. 2.2 shows that when substrate concentration is less than 20 mM/L, specific growth rate is the highest with pH=6.0 followed by pH=6.5 and pH=7.0. With increase in substrate concentration, specific growth rate of microorganisms become higher with increase in pH from pH=6.0 to pH=7.0.

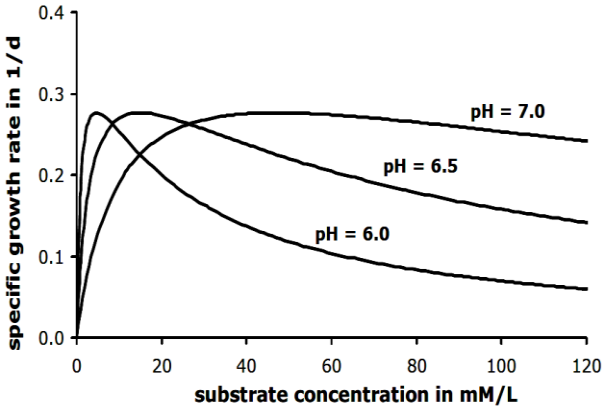


Fig. 2.2 Maximum specific growth rate for different pH values [Andrews and Graef, 1971]

2.2.7 EFFECT OF HYDRAULIC RETENTION TIME (HRT) ON BIOGAS PRODUCTION

HRT is defined as the average time spent by the input slurry inside the digester before it comes out of it. HRT varies between 20-120 days depending upon the design and operating condition of the digester. HRT taken in tropical areas like India is generally 40-50 days. HRT in cold climatic countries like U.K., Canada and China is taken to be 100 days [Mittal, 1996].

Linke, 2006 presented that gas production varies with HRT as per following relationship.

$$p = \frac{HRT.k}{HRT.k + 1} \tag{2.2}$$

where

p = y/y_m= biogas yield with respect to maximum yield

y= gas production at any HRT

y_m= maximum gas production

k = the first order kinetic constant

Figure. 2.3 present the biogas production with HRT for different kinetic constants. Biogas yield increases with HRT for all the values of kinetic constant. Moreover, increase in kinetic constant increases biogas yield for a specific HRT.

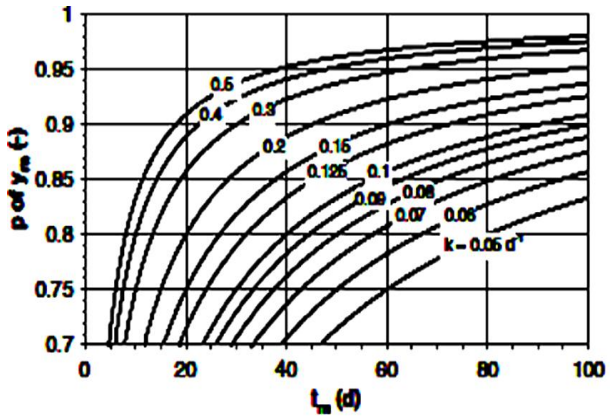


Fig. 2.3 Effect of HRT on biogas production for different value of kinetic constant [Linke, 2006]

2.2.8 EFFECT OF MECHANICAL STIRRING AND AGITATION ON BIOGAS YIELD

A mechanical stirrer facilitates the diffusion of the bacteria throughout the slurry, thus exposing them homogenously to the undigested material [Karim and Hoffmann, 2005].Further, it helps in mixing the fresh organic material and nutrients with the slurry already retained in the digester. Stirring also helps in better temperature distribution enabling the microbial communities to thrive [Burton and Turner, 2003; Ward et al., 2008]. Agitation helps in the release of gas bubbles trapped in the medium and prevents sedimentation of denser material on the bottom of the reactors well as preventing the formation of scum layers [Mahanta et al., 2005]. Ratusznei et al., 2001 reported that mixing enhances the overall digestion rate by improving the mass transfer fluxes. The stirring improves the particle suspension and increases the solubility of the solid organic matter in suspension in the digestate [Pinho et al., 2004]. Mahanta et al., 2004 experimented in IIT Guwahati and found that recirculation of digestate increases the gas production by three times as compared to that of without agitation.

2.2.9 EFFECT OF ADDITIVES ON BIOGAS PRODUCTION

Kumar et al., 1987 experimented to see the effect of additives on biogas production and found that 5% of commercial charcoal addition to cattle dung on dry weight basis increased the production of biogas by 17% and 35% in batch and continuous processes, respectively.

Geeta et al., 1986 studied the effect of additives on biogas production. They used vermiculite, charcoal and lignin to bovine excreta as feed material and observed the increase in gas production by 15-30%.

2.2.10 EFFECT OF TOXICITY ON BIOGAS PRODUCTION

A small quantity of mineral ions (e.g. sodium, potassium, calcium, magnesium, ammonium and sulphur) are needed to stimulate the growth of bacteria, but the same mineral ions in heavy concentrations produce toxic effect inhibiting the growth of bacteria. Heavy metals (e.g. copper, nickel, chromium, zinc, lead, etc.) in small concentration help in the normal growth of bacteria but in high concentration, the same heavy metals have toxic effects [Youngsukkasem et al., 2013]. Mohanrao, 1975 reported that detergents, antibiotics, organic solvents etc. inhibit the growth of bacteria and therefore addition of these substances in the digester are to be avoided to have good biogas production.

2.2.11 INFLUENCE OF TOTAL SOLID (TS) ON BIOGAS PRODUCTION

Many researchers had reported that TS of the feed stock plays an important role in production of biogas. Fresh cattle wastes consist of 20% TS and 80% water. TS again contain 70% volatile solids and 30% fixed solids. Since, 8 to 10% TS in feed is required to yield optimum amount of gas through anaerobic digestion, fresh cattle dung is diluted with water in 1:1 ratio. If required this ratio can vary from 1:1.25 to 1:2 ratios [TERI, 1987]. Hills and Roberts, 1981 reported that the performance of digesters containing dairy manure and field crop residues is the maximum when the TS of the slurry were 8%. Budiyono et al., 2010 stated that TS content of 7.4 and 9.2% in cattle dung exhibit the best performance for digestibility. Mahanta et al., 2004 reported that for cattle dung the maximum gas production was obtained with 8% TS.

2.3 INFLUENCE OF BIOFILM CARRIER ON BIOGAS PRODUCTION

Support media provide a surface on which microbial biofilms can attach and grow, increasing digester stability increasing the population of the microorganisms inside the digester. Biofilms form on the substrates and enhance the digestion increasing the OLR (Organic Loading Rate). This decreases COD (Chemical Oxygen Demand) leading to high rate of biogas production [Mshandete et al., 2008].

Andersson and Björnsson, 2002 investigated on different support media and found that the use of straw as support media increases methane production than glass or plastic carriers. Yang et al., 2004 reported that synthetic materials such as loofah sponge, rock wool and polyurethane foam

have been found to be effective support media. A comparative study by Mshandete et al.,2008 looked into the effectiveness of waste sisal fibers, pumice and glass beads as biofilm carriers and found that sisal fibres was the most effective one among these materials. Pinho et al., 2004 reported that support media made of polyurethane matrices in batch reactor along with mechanical stirring improves biogas production.

Studies suggest that effective biofilm carriers have a rough uneven surface with crevices, microscopic ridges and pores, which are good for attachment of bacteria. Biochar shows a rough, highly porous surface area, with both micro and macro structures that will allow organisms to adhere to their surface. Indeed the size of the pore structure will determine whether biofilms develop only on the surface or also within the internal structure of the char; this pore size can be controlled in its production. These characteristics make biochar a potential candidate as a cheap and available resource for microbial cell immobilization in anaerobic digesters [Lehmann et al., 2011].

2.4 PRETREATMENT OF BIOMASS

Lignocellulosic biomasses are rich in cellulose, hemicellulose and lignin. Their digestibility is low due to their cross linked structure and high lignin to cellulose ratio. The digestibility of biomass can be improved by pretreatment [Palmowski, and Müller, 1999; Fan et al., 1988]. Pretreatment involve the alteration of cellulose structure of the biomass rendering fast hydrolysis of both the cellulose and hemicellulose producing biogas in short span of time. Various pretreatment methods that can be applied include mechanical/physical, chemical and biological pretreatment.

The most significant physical pretreatment include the particle size reduction [Fan et al., 1988], which eventually leads to the increase in available surface area and the release of intracellular components [Palmowski, and Müller, 1999, Lehtomaki, 2006]. Sharma et al., 1988 had reported significant increase in biogas production with decrease in particle size of feed materials. They worked on agricultural and forest residues such as wheat straw, rice straw, mirabilis leaves, cauliflower leaves, ipomoea fistulosa leaves, dhub grass and banana peeling with different particle sizes and found that particle sizes of 0.088 and 0.4 mm produced an almost equal quantity of biogas and it was higher than that of the particle sizes 1 and 6 mm, respectively.

2.5 DESIGN AND PERFORMANCE OF ANAEROBIC DIGESTERS

Anaerobic Digestion is a process that involves the decomposition of organic waste like food, agricultural and human wastes by bacteria in an environment without oxygen to produce biogas. Anaerobic digestion has been successful in reducing large quantities of waste going to landfill, decreasing emissions of greenhouse gases and creating organic fertilizer. This process addresses two major issues involving waste management and harnessing of renewable energy.

Singh and Anand, 1994 conducted comparative study on performance of solid state cylindrical digesters with conical structure at the bottom and floating drum gas holder similar to a conventional KVIC digester at the top. The maximum ambient temperature was 40.2°C and minimum temperature was 24.9°C. They found that the biogas yield of the solid state digester (SSD) was 84% of that of the conventional digester and the same was observed due to the variation in ambient temperature which directly affects the performance of the above-ground SSD.

Mahanta et al., 2004 investigated the effect of partitioned wall in fixed dome type biogas digester and found that biogas production was more in the partitioned wall digester compared to the without partition wall digester as the operational retention time was more in case of partitioned wall digester which allowed better digestion of the input material.

Nielson and Mladenovska, 2004 reported the performance of two-stage digester consisting of a digester operating at 68°C with HRT of 3 days and connected to another digester at 55°C with HRT 12 days for digestion of cattle manure and compared with a conventional single-stage thermophilic digester at 55°C with HRT 15 days. They observed that when an organic loading of 3 g volatile solids (VS) per liter per day was applied, the two-stage setup had a 6% to 8% higher specific methane yield and 9% more effective VS-removal than the conventional single-stage reactor.

Various methods are adopted by different researchers for improving the performance of anaerobic digester. They are classified as thermal, mechanical and chemical- microbiological methods.

2.6 METHODS INVOLVING THERMAL MANAGEMENT OF DIGESTER

Biogas production increases with increase in substrate temperature [Tiwari et al., 1988]. Several researchers had reported that microbes cannot tolerate the thermal stress [Beba, 1988; Subramanyam, 1989]. Thus it is required to maintain the temperature of digestate or substrate within $\pm 1^{\circ}C$ inside the digester.

2.6.1 INSULATION OF DIGESTER

To produce maximum biogas from anaerobic digestion process it is essential to maintain temperature in the range of mesophilic or thermophilic range. For maximum production of biogas the optimum temperature of cattle slurry is $37^{\circ}C$ in mesophilic digestion process which is difficult to achieve naturally specially during winter [Tiwari et al., 1992]. During winter atmospheric temperature become very low which eventually led to the decrease in slurry temperature in the digester. In that case, insulation of the digester is a good option to reduce heat loss from it [Tiwari et al., 1988]. Insulating the digester with material like straw, tirpal etc. the heat loss from the digester can be avoided [Tiwari et al., 1988]. Tiwari et al., 1988 had reported improvement in temperature of digester and gas production with surface glazing and cover with insulation (Tirpal) during off-sunshine hours.

Figure. 2.4 shows that using glazing as well as movable insulation, temperature of the slurry of the conventional biogas plant could be maintained at 29°C, whereas using only glazing without insulation temperature of the slurry was maintained at 25°C. Temperature of the slurry of the biogas plant without glazing and insulation was maintained at 21°C.

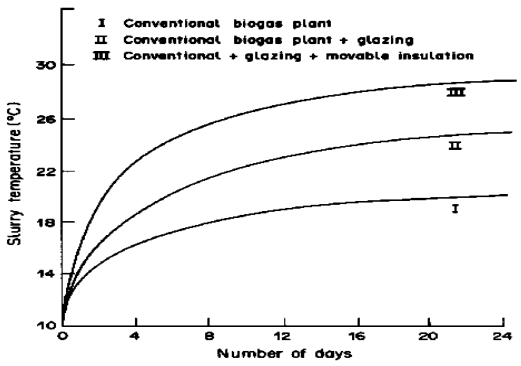


Fig. 2.4 Variation of slurry temperature with number of days [Tiwari et al.,1988]

2.6.2 HEATING OF DIGESTER SUBSTRATE

Methane forming bacteria are heat sensitive anaerobic microorganisms [Beba, 1988]. That is why; production of biogas is insignificant when the temperature of slurry falls below 15°C [Meynell, 1976]. In order to attain optimum biogas production, it is necessary to heat up the input slurry. Heating the input slurry can be done by using either solar energy [Gupta et al., 1988] or a heat exchanger [Beba, 1988]. However, Overheating should be avoided as it may kill bacteria [Subramanyam, 1989].

Gupta et al., 1988 conducted transient analytical study of solar assisted fixed dome type biogas plant. They proposed the use of water heater system with sufficient number of collectors in series to improve the substrate temperature for use in winter season so as to generate more gas. Improvement in performance with insulation on the walls and base of the digester is also reported by them. Figures 2.5 and 2.6 present the variation of substrate temperature with number and length of collectors.

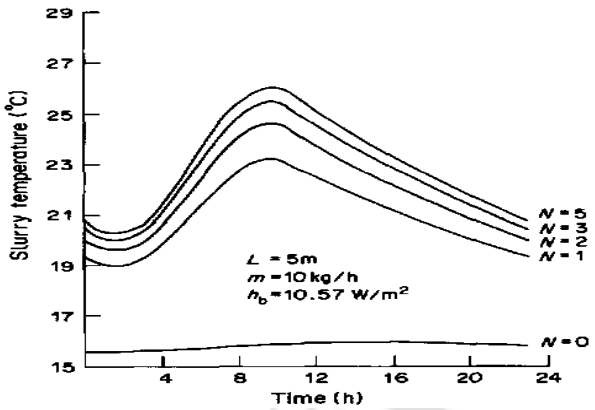


Fig. 2.5 Hourly variation of substrate temperature with number of collectors [Gupta et al., 1988]

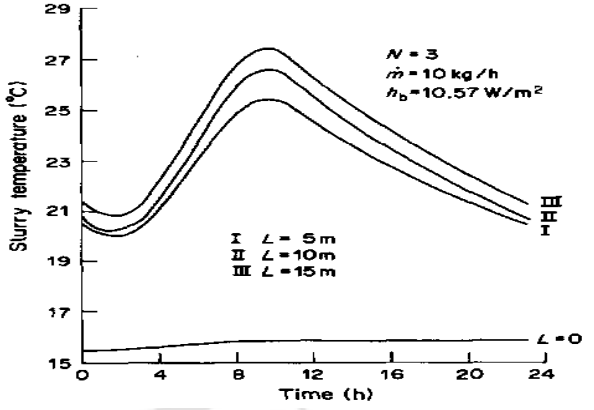


Fig. 2.6 Hourly variation of substrates temperature with length of pipe [Gupta et al., 1988]

2.6.3 SOLAR HEATING OF DIGESTER

To prevent heat loss from the digester or from the slurry inside digester a plastic tent can be erected over the digester, making the joints airtight. It creates greenhouse effect on the plant. Yadav et al., 1987 studied the KVIC biogas plant and incorporated the greenhouse and water heater concept in its design of the digester. Fig. 2.7 shows that with application of water heater,

solar canopy and movable insulation slurry temperature increases. Slurry temperature of conventional biogas plant with water heater, solar canopy and movable insulation was the highest followed by conventional biogas plant with water heater and solar canopy, then conventional biogas plant with water heater as compared to a conventional biogas plant without any aid.

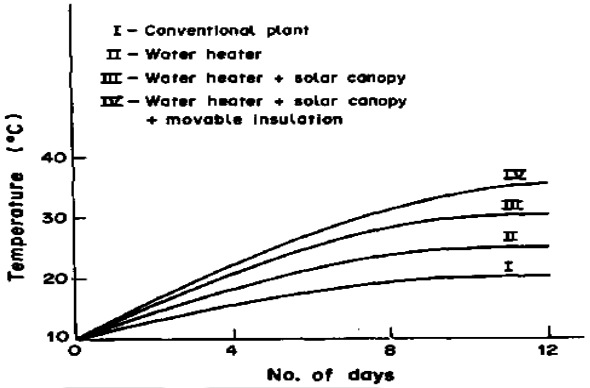


Fig. 2.7 Transient behaviour of slurry temperature with time [Yadav et al., 1987]

2.7 KINETIC MODELING STUDY

The kinetics of biodegradation processes is very important to know about the performance of reactors. It helps in designing the biogas plant for various feed materials. It also helps in understanding the mechanisms behind anaerobic digestion process [Mata-Alvarez et al., 1993].

Different mathematical models based on various parameters have been reported in literature. It is interesting to note that most of the kinetic models were reported based on cattle dung as substrate. A few models based on substrates other than cattle dung is reported as well. Some of them are discussed below.

2.7.1 KINETIC MODELS BASED ON BIOGAS PRODUCTION

Buswell and Muller, 1952 model predicted that the production of methane and carbon dioxide can be calculated if the chemical composition of the organic matter is known [Gerber and Span, 2008]. The following is the Buswell and Muller, 1952 model which include carbon, hydrogen and oxygen in the chemical reaction so that methane and carbon dioxide can be calculated from the reaction.

$$C_aH_bO_c + \left(a - \frac{b}{4} - \frac{C}{2}\right)H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{C}{4}\right)CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{C}{4}\right)CO_2 \quad (2.3)$$

This model suggests that the yield of methane in percentage by volume depends upon the type of substrates used as input. For example, 50% methane yield can be obtained from glucose degradation as shown in Eq. 2.4.

$$C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2 \quad (2.4)$$

A modification and improvement of the Buswell and Muller, 1952 model is the Boyle model. He included nitrogen and sulphur in the model so that fraction of the ammonia and hydrogen sulphide can also be calculated [Gerber and Span, 2008].

$$C_aH_bO_cN_dS_e + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3.d}{4} + \frac{e}{2}\right)H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3.d}{8} - \frac{e}{4}\right)CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3.d}{8} + \frac{e}{4}\right)CO_2 + dNH_3 + eH_2S \quad (2.5)$$

Hashimoto et al., 1981 developed a kinetic equation for methane fermentation in terms of several parameters. According to this model, for a given loading rate (S_0/θ), volume of methane production per volume of digester per day depends upon the biodegradability of the material (B_0) and the kinetic parameters μ_m and *K*.

$$r_v = \frac{B_0.S_0}{\theta}\left[1 - \frac{K}{\theta\mu_m - 1 + K}\right] \quad (2.6)$$

where

r_v= volumetric methane production rate, LCH_4/L fermentor /day

S_0 = influent total volatile solids (VS) concentration, g/L

B_0 = ultimate methane yield, $LCH_4/g.VS$ added as $\theta \rightarrow \infty$

θ = hydraulic retention time, day

μ_m = maximum specific growth of microorganisms, per day

k = kinetic parameter, dimensionless

Chukanov et al., 2005 used the Chen-Hashimoto, 1978 and Chen and varel, 1980 model and developed a modified form of model to apply it to the optimization of the methane fermentation of cattle dung.

The modified form of the model is:

$$G = B_0 \times 2.6\times10^3\left(1-\frac{k}{\mu_{max}\theta-1+k}\right) \quad (2.7)$$

$$Y_V = \left(\frac{P}{2.6\times10^3}\right)\times\left(\frac{S_0}{\theta}\right) \quad (2.8)$$

$$V = \theta.\frac{2.6\times10^3}{S_0} \quad (2.9)$$

$$Q = B_0.2\times10^2\left(1-\frac{k}{\mu_{max}\theta-1+k}\right) \quad (2.10)$$

where

G = total methane output from the fermentor (dm^3/day)

Y_v = the methane output per unit of fermentorvolume per day

V = volume of the fermentor (m^3)

Q = degree of degradation of the organic matter (%)

B_0= maximum methane output per unit of organic matter in the substrate (dm^3 CH_4/gVS)

S_0= concentration of the organic matter of the substrate (gVS/ dm^3)

θ =HRT in days

k=kinetic rate constant

μ_{max} = maximum specific growth rate of the microorganism

2.7.2 KINETIC MODELS BASED ON BACTERIAL GROWTH

In 1940, Monod studied the growth of bacterial cultures and developed a hyperbolic relationship between the specific microbial growth rate and limited substrate concentration [Monod, 1940]. According to this model, the specific growth rate of micro-organisms is given by Eq. 2.11.

$$\mu = \mu_{max} \cdot \frac{S}{k_S + S} \tag{2.11}$$

where

μ = specific growth rateof microorganisms

μ_{max} = maximum specific growth rateof microorganisms

k_s = Monod kinetic constant

S = substrate concentration

Figure 2.8 shows dependency of specific growth rate on substrate concentration according to Monod model. From the figure it is observed that the specific growth rate of micro-organism increases monotonically with substrate concentration. However, the specific growth rate saturates for higher concentration of substrates. Figure 2.8 reveals that when specific growth rate, $\mu = \frac{\mu_{max}}{2}$, substrate concentration, $S=K_s$ (Monod kinetic constant).

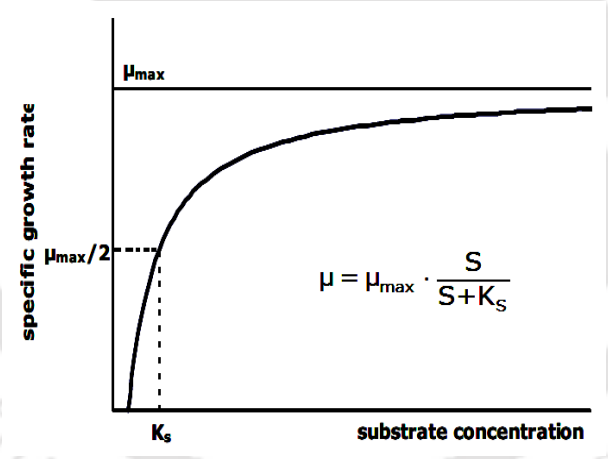


Fig. 2.8 Specific growth rate depending on substrate concentration [Monod, 1940, Gerber and Span, 2008]

Major drawback of the Monod model is that due to the use of a single kinetic parameter, the bacterial reactions are difficult to describe at extreme hydraulic retention times (low or high HRT).

Contois, 1959 studied the continuous cultures of aero-bactoraerogenes growing in chemically defined media and found that specific growth rate (μ) is a function of population density (*p*) and limiting substrate concentration (*S*) as given by Eq. 2.12.

$$\mu = \frac{u_m S}{Bp + S} \tag{2.12}$$

where

μ = specific growth rate

p = population density

S = substrate concentration

u_m and B are the growth parameters and are constants under defined conditions

Contois, 1959 stated that this equation serves as adequate model for bacterial growth in both batch and continuous cultures and is claimed to be realistic.

Zwietering et al., 1990 modified the Gompertz model by substituting the mathematical parameters of the model by some parameters with biological meaning. This was done by deriving an expression of the biological parameters as a function of the basic function and then substituting them in the formula.

$$y = A.\exp\left\{-\exp\left[\frac{\mu_m.e}{A}(\lambda - t) + 1\right]\right\} \tag{2.13}$$

where

y = overall bacterial growth

A = bacterial growth potential

μ_m = the maximum specific growth rate

2.7.3 KINETIC MODELS TO CALCULATE HYDRAULIC RETENTION TIME (HRT)

The Chen-Hashimoto model, (1978, 1980) based on Contois model for a completely mixed, continuous flow system is given by Eq. 2.14.

$$\theta = \theta_{MIN} + \theta_{MIN}\ k\left[\frac{B}{(B_0 - B)}\right] \tag{2.14}$$

where

B = the volumetric methane yield (LCH_4/g VS added) after limited time

B_0= the volumetric methane yield (LCH_4/g VS added) after infinite time

k = kinetic rate constant

θ = hydraulic retention time (HRT) (days)

θ_{MIN} = minimum time required for gas production

All the models discussed above are based on cattle dung as substrate. It is observed that models based on substrates other than cattle dung is not very plenteous. Also very few models based on effect of temperature on biogas production are reported in literature.

Few models based on substrates other than cattle dung is reported below. Linke, 2006 developed one kinetic model based on mass balance and first order kinetic which can be applied for dimensioning completely stirred tank reactors (CSTR) digesting organic waste from food processing industries, animal waste slurries or biogas crops. According to this model, the hydraulic retention time, HRT and VS biogas yield, y for a CSTR can be described as:

$$\theta = \frac{1}{k}\left(\frac{y}{y_m - y}\right) \tag{2.15}$$

$$y = \frac{\theta k y_m}{\theta k + 1} \tag{2.16}$$

where

θ = hydraulic retention time, HRT (day)

k = the first order kinetic rate constant (day^{-1})

y = biogas yield

y_m= the maximum VS biogas yield

The values of k and y_m are the specific parameters for different substrates used and can be found experimentally.

Liquerica et al., 1984 derived expressions from the Chen-Hashimoto model, 1978 and 1980 to correlate the VS concentration of effluent (S), biodegradable conversion efficiency η, and the volumetric substrate utilization rate, F for the methane fermentation from straw as given below:

$$\frac{S}{S_0} = R_c + \frac{(1-R)k}{\mu_m \theta - 1 + k} \tag{2.17}$$

$$\eta = \frac{\mu_m \theta - 1}{\mu_m \theta - 1 + k} \times 100 \tag{2.18}$$

$$F = \frac{(1-R)S_0}{\theta}\left(1 - \frac{k}{\mu_m \theta - 1 + k}\right) \tag{2.19}$$

where

R_c is the refractory coefficient (non-biodegradable VS/total VS)

k is kinetic rate constant

S is the effluent substrate concentration

S_0 is the influent substrate concentration (g VS/l)

2.7.4 MODELS BASED ON INFLUENCE OF TEMPERATURE

Temperature is the most important ambient condition for bacterial growth [Ingraham, 1962]. Actually the reaction rate in chemical processes increases with temperature [Gerber and Span, 2008]. In most of the mathematical model the effect of temperature in anaerobic digestion is given by Arrhenius Equation.

$$k = f \exp\left(-\frac{E_a}{RT}\right) \tag{2.20}$$

where

k= the rate constant

f= the pre exponential factor

T = the temperature

R = the universal gas constant

E_a= the activation energy.

Sinclair and Kristiansen, 1993 formulated a model for anaerobic digestion processes based on Arrhenius equation which shows the effect of temperature on biogas production.

$$\mu_{\max}(T) = k_1 . \exp\left(-\frac{E_1}{R.T}\right) - k_2 . \exp\left(-\frac{E_2}{R.T}\right) \tag{2.21}$$

Figure 2.2 shows the effect of temperature on bacterial growth. It shows that with increase in temperature from 20°C to 35°C, specific growth rate of micro-organisms increases. After that

with increase in temperature from 35°C to 45°C specific growth rate of microorganisms decreases.

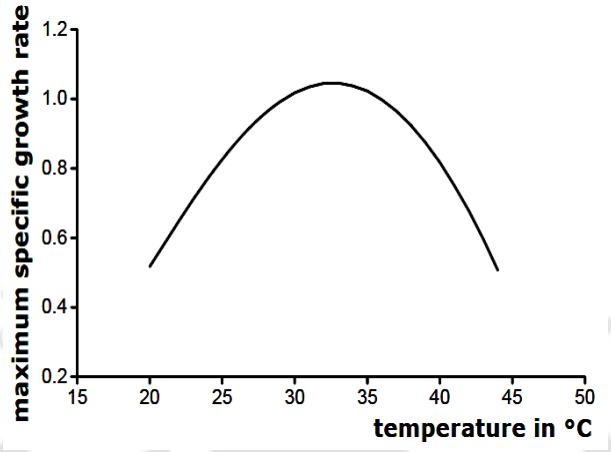


Fig. 2.9 Maximum specific growth rate depending on temperature [Sinclair and Kristiansen, 1993]

2.7.5 KINETIC MODELS TO SIMULATE BIOGAS ACCUMULATION

Several researchers have reported about the simulations of biogas, methane and hydrogen production rate and accumulation in their reports (Altas, 2009; Li and Fang, 2007; Lin and Shei, 2008; Bilgili et al., 2009; De Gioannis et al., 2009; Kumar et al., 2004; Tosun et al., 2008; Wang and Wan, 2009; Erses et al., 2008; Mu et al., 2007; Li et al., 2008).

Due to the involvement of bacteria in the anaerobic digestion process, kinetic models particularly the first order kinetics were commonly applied to simulate the anaerobic biodegradation [Lo et al., 2011]. Like the growth of bacterial population, biogas production rate showed a rising limb and a decreasing limb which was indicated by exponential and linear equation (De Gioannis et al., 2009; Kumar et al., 2004).

The biogas accumulation can be simulated by logistic growth curve, exponential rise to maximum as well as modified Gompertz equations which were commonly used in the simulation of methane and hydrogen production (Altas, 2009; Li and Fang, 2007; Lin and Shei, 2008; Wang and Wan, 2009). Lo et al., 2010 simulated cumulative biogas production from anaerobic digestion of MSW using exponential rise to maximum and modified Gompertz equations and found that Modified Gompertz plot had higher correlation than exponential rise to maximum plot for simulating cumulative biogas production.

Many other researchers have applied the modified Gompertz equation in their work [Agulanna et al., 2012; Nopharatana et al., 2007; Yusuf et al., 2011]. Budiyono et al., 2010 have applied modified Gompertz equation to study the biogas production from cattle dung. Momirlan and Veziroglu, 1999, Zwietering et al., 1990 and Lay et al., 1996, 1998 applied modified Gompertz equation to study the bacterial growth.

2.8 CARBON DIOXIDE REMOVAL FROM BIOGAS

A major component of biogas is carbon dioxide and it is non-combustible. It lowers the calorific value of biogas. Calorific value of biogas with CO_2 varies from 18.7 to 26 MJ/m^3 and that of without CO_2 is between 33.5 to 35.3 MJ/m^3. That is why to use the biogas successfully it is very important to remove the carbon di-oxide from it. Also, after removing the carbon dioxide biogas can be directly fed to a CHP unit to produce electricity and heat [Monnet, 2003]. Various methods are developed by researcher which is now commercially being used for removal of carbon-di-oxide [Kapdi et al., 2005]. They are discussed below.

2.8.1 PHYSICAL ABSORPTION

This method is based on the principle that carbon-di-oxide as well as hydrogen sulphide are more soluble in water than methane at high pressure. In this method pressurized biogas is fed to the bottom of a packed column and water is fed from top to operate it counter-currently for better absorption [Wellinger and Lindberg, 1999].

Shannon, 2000 used water scrubbing method for removal of carbon-di-oxide as well as hydrogen sulphide. He stated that this is the easiest and the cheapest method of biogas purification system. He compressed biogas and fed to the packed bed column from bottom and water was sprayed from top in a counter-current manner. Recycling of water was also done.

Ofori-Boateng and Kwofie, 2009 studied the most common three biogas purification method, water scrubbing, chemical absorption and biological method and found that water scrubbing was the most simple, low cost, eco-friendly and suitable method for enrichment of biogas in Ghana. Their proposed design removed 93% v/v of carbon-dioxide from the raw biogas.

Bhattacharya et al., 1988 designed a water scrubbing system which provided 100% pure methane but the actual percentage of methane in the upgraded biogas was dependent on some

factors like dimensions of scrubbing tower, gas pressure, and composition of raw biogas, water flow rates and purity of water used.

Vijay, 1989 developed a packed bed type scrubbing system which removed 30-40% more CO_2 by volume compared with the scrubbing without a packed bed. He used locally available packing materials for the scrubbing system.

Vijay et al., 2006 designed a water scrubbing system for CO_2 removal from raw biogas which could remove CO_2 from biogas upto 99% at gas flow rate of 1.5 m^3/h, water flow rate of 1.8 m^3/h and at the inlet gas pressure of 1.0 MPa. Vijay, 2009 experimented on water scrubbing system in IIT Delhi for enriching biogas by removing CO_2, H_2S and water vapors and obtained purified biogas with methane content upto 90-95%.

Khapre,1989 designed a continuous counter-current type scrubber which reduced CO_2 content from 30% at inlet to 2% at outlet by volume with gas flow rate of 1.8 m^3/h at inlet gas pressure of 0.48 bar and water flow rate of 0.465 m^3/h.

Dubey, 2000 performed experiment on three water scrubbers whose diameters were 150 mm (height: 1.5 m), 100 mm (height: 10 m) and 75 mm (height: 10 m) to absorb CO_2 (37-41%) present in the biogas and found that the CO_2 absorption depends upon the flow rates of gas and water rather than the different diameters of scrubbers.

Shyam, 2002 from G.B. Pant University of Agriculture and Technology, Patnagar, India designed a scrubbing tower of height 6 m which is packed upto a height of 2.5 m with spherical plastic balls of diameter 25 mm. The raw biogas compressed at a pressure of 5.88 bar was passed at a flow rate of 2 m^3/h while water was circulating through the tower. The scrubbing tower could remove CO_2 content upto 87.6% from the raw biogas.

2.8.2 CHEMICAL ABSORPTION BY CAUSTIC SCRUBBING

It is based on the principle that when caustic solution reacts with CO_2, there occurs an irreversible carbonate-forming reaction followed by a reversible bicarbonate-forming reaction. Generally regeneration of spent bicarbonate solution is not done due to high steam requirement. It involves the use of hydroxides of sodium, potassium and calcium.

$$2\ KOH + CO_2 \rightarrow K_2CO_3 + H_2O \quad (2.22)$$

$$K_2CO_3 + CO_2 + H_2O \rightarrow 2\ KHCO_3 \quad (2.23)$$

Savery et al., 1972 reported that three agents NaOH, KOH and $Ca(OH)_2$ can be used in chemical scrubbing of biogas for removal of CO_2. The rate of absorption of CO_2 in alkaline solution is assisted by agitation and the concentration of the solvent. The rate of absorption is rapid with NaOH at normalty of 2.5-3.0. Tippayawong and Thanompongchart, 2010 experimentally investigated Chemical absorption of CO_2 and H_2S by aqueous solutions of sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$) and mono-ethanolamine (MEA) in a packed column at different gas to liquid flow and they found that the aqueous solutions could remove CO_2 from biogas upto 90%.

2.8.3 SCRUBBING BY AQUEOUS SOLUTION OF MEA

In this method, biogas is purified by passing it through an aqueous solution of mono-ethanolamine (MEA). The advantage of this method is that MEA solution can be completely regenerated by boiling it for 5 minutes.

Biswas, 1977 developed a method of CO_2 scrubbing by passing biogas through a 10% aqueous solution of mono-ethanolamine (MEA) in a column of height 15 cm and diameter of 5 cm respectively with an orifice. Gas flow rate was 100 ml/min. Initial pressure of gas was 10 cm of water column and drop in pressure head was 5 cm of water column. In this method CO_2 content of biogas was reduced to 0.5-1%.

2.8.4 ADSORPTION ON A SOLID SURFACE

Pressure swing adsorptions (PSA), temperature swing adsorption (TSA) are some of the techniques applied for carbon-dioxide removal from high pressure biogas based on the principle of adsorption on solid surface. CO_2 separation from methane is done by adsorption/desorption of CO_2 on zeolites or activated carbon at different pressure levels. By proper choice of adsorbents (e.g. activated carbon, silica, silicates, alumina which is known as molecular sieves.) this method can be used to remove CO_2, H_2S, moisture and other impurities. It has a good gas and moisture removal capacity, simple design and is easy to operate. Adsorption takes place generally at

elevated temperature and pressure. But due to high Pressure drop and high heat requirement it becomes an expensive process [Wise, 1981].

Molecular sieves, activated carbon, natural zeolites are used as sorbents in PSA technique [Siriwardane et al., 2001, 2003]. Schomaker et al., 2000 reported that CO_2 can be removed from biogas by pressure swing adsorption method. They used three active carbon beds. One of the beds was fed with biogas. Under pressure 6 bars CO_2 got adsorbed. When there is saturation of CO_2 in the adsorption bed, the process is shifted to the second bed. The saturated bed is depressurized to ambient pressure. The efficiency of the process is upto 98%. Pandey and Fabian, 1989 used naturally occurring zeolite-Nepolian Yellow Tuff (NYT) for adsorption. They found that the active component for CO_2 adsorption is chabazite, which has adsorption capacity of 0.4 kg CO_2 per kg of chabazite at 1.5 bars and 22°C. During the adsorption process the H_2S content is also reduced.

Alonso-Vicario, 2010 studied the removal of CO_2 from biogas by pressure swing adsorption (PSA) with thermal desorption using two synthetic molecular sieves and a natural zeolite (Clinoptilolite) as adsorbent material. The experimental results indicate that Clinoptilolite is the best material choice for purification and upgrading of biogas.

2.8.5 MEMBRANE SEPARATION

The membrane separation method is based on the principle that some components of raw biogas get transported through a thin membrane (<1 mm) due to difference in partial pressure while others are retained. It is highly dependent on the permeability of the component in the membrane material. In order to obtain high methane purity, the difference in permeability of methane and carbon dioxide must be high.

Hagen and Polman, 2001 reported that solid membrane constructed from acetate-cellulose has 20 times higher permeability of CO_2 than CH_4 and that 60 times higher permeability of H_2S than CH_4. Operating pressures are kept in the range of 25-40 bar.

Wellinger and Lindberg, 1999 used two basic systems of gas purification using membranes. One is high pressure gas separation with gas phases on both sides of the membrane and a low-

pressure gas liquid absorption separation where a liquid absorbs the molecules diffusing through the membrane. In both the cases raw gas was upgraded to 96% pure methane.

Harasimowicz et al., 2007 showed that using the capillary module with polyimide membranes it was possible to achieve the enrichment of methane from the concentrations of 55–85% up to 91–94.4%. Permeability of carbon di-oxide in polyimide membrane is 13-fold higher than of methane gas. The membrane material was resistant to the small concentrations of sour gases and assured the reduction of hydrogen sulphide and water vapor concentrations, as well.

2.8.6 CRYOGENIC SEPARATION

The cryogenic method of purification is based on the principle that gaseous mixtures can be separated by fractional condensation and distillation at low temperature. It allows recovery of pure components in the form of a liquid which can be transported conveniently.

Los Angeles County Sanitation District and the Cryenco Engineering Company of Denver, Colo. attempted to apply the cryogenic process for the removal of CO_2 from digester gas but could not make it successful. Rather complicated flow schemes got involved and thermal efficiency became low. Capital cost and utility requirements were also very high in this process [Wise, 1981]. Hagen and Polman, 2001 reported that using cryogenic separation method more than 97% methane could be obtained in the biogas.

After a thorough literature study on all the processes of carbon dioxide removal from biogas, the advantages and disadvantages of the processes are summarized as shown below in Table 2.4.

Table 2.4. Advantages and disadvantages of carbon dioxide removal process

Sl. No.	Processes	Advantages	Disadvantages
1	PSA	Economy in production with comparatively high purity. Capital costs are moderate. Relatively quick installation and start up.	Not much scalability in production. Equipment maintenance on the higher side, high pressure and Chemical regeneration is required.
2	Water scrubbing	Simple process, remove both H_2S and CO_2 using a water stream.	High pressure, difficulty in recovery of CO_2.
3	Cryogenic	High purity	Capital cost high. Requirement of large sites. Longer start-up and shut down process. Limited scalability in production.
4	Membrane	Fast installation and start up. Production of output is flexible. Purity and flow rate can vary.	Economically not viable. Not suitable for high purity needs. Consumes relatively more electricity per unit of gas production.
5	Chemical absorption	The chemical absorbents are more efficient in low pressure.	Regeneration of the solvents requires a relatively high energy input. Disposal of by product formed due to chemical reaction is a problem.

2.9 SUMMARY

An extensive literature review has been carried out on various factors affecting the biomethanation processes, effect of different feed material on biogas production, biofilm carrier, pretreatment of biomass, design and performance of digester, kinetic modeling study, carbon dioxide removal processes, etc. It is observed that most of the experiments were performed on cattle dung whereas there are plenty of lignocellulosic bio-wastes with high cellulose content and volatile matter content are available in most of the developing countries which has got high potential to generate biogas. Very few literatures have been found on biogas production from lignocellulosic biomasses [Petersson et al., 2007; Wu et al., 2010] which requires further research in terms of process and digester development.

Various mathematical models based on different parameters are reported in literature [Gerber and Span, 2008; Linke, 2006], but kinetic models based on temperature is very few [Sinclair and

Kristiansen, 1993] and are specific to mesophilic anaerobic digestion. Kinetic models based on thermophilic anaerobic digestion are hardly found in the literature. Further, models taking care of biogas production with lignocellulosic biomass are also few. Although temperature is the most important ambient condition for bacterial growth [Ingraham, 1962], temperature dependency of biogas digestion is not that revealing in most of the models.

It is observed from the literature that anaerobic digestion can be improved by using support media so as to retain the methanogenic bacteria for long time in the digester [Pinho et. al, 2004]. However, research towards the same is hardly reported. Various biogas purification methods are reported in literature. But most of the processes are stated to be very expensive and needed high gas pressure.

Hence, based on the literature review it is proposed to identify and collect lignocellulosic biomass available locally and check their potentiality for biogas production. It is also proposed to conduct parametric as well as kinetic study on the selected lignocellulosic biomass for biogas yield. Effect of temperature, being one of the important parameters on gas yield has also been considered in the studies. Moreover, it is planned to design and develop a cheap, easy to operate biogas purification method for carbon di-oxide removal process. In the following chapter (Chapter 3) the characterization of the selected lignocellulosic biomass collected from the North Eastern Region of India is presented.

CHAPTER 3

CHARACTERIZATION OF BIOMASS

3.1 INTRODUCTION

Lignocellulosic biomasses are recognized to be potential feed material for production of biogas. They are available in plenty throughout the world. Cellulose, hemicellulose and lignin are the three major constituents of lignocellulosic biomass. The other components such as water and proteins do not participate in forming the structure of the material [Raven et al., 1992]. The cellulose maintains the crystalline fibrous structure as the core of the complex. Hemicellulose is located between the micro- and macrofibrils of cellulose. Fig. 3.1 shows the fibre content present in the biomass.

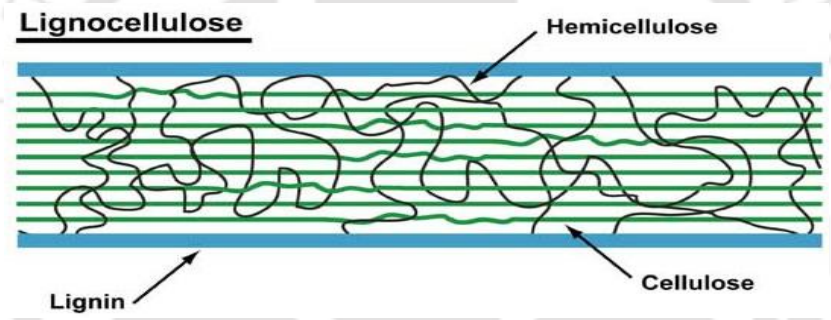


Fig. 3.1 Fibre constituents in biomass [Faulon and Carlson, 1994]

Lignin is responsible for the structural role of the matrix in which the cellulose and hemicellulose is bounded [Faulon and Carlson, 1994]. Approximately 44% of the fermentable materials are shielded by lignin [Robbins et al., 1979]. Due to poor degradation of lignin in anaerobic condition, the rate and extent of digestion of lignocellulosic material become incomplete [Fan et al., 1988]. They are hardly used for production of biogas, rather they are disposed of in the open environment causing serious pollution problem and health hazard. Proper identification of the specific biomass is essential to estimate the biogas production. Hence identification and characterization of biomass plays a vital role to determine the biogas production potential. In the present work a total of fifteen biomasses available in the North Eastern Region of India are collected and characterized. Based on the characterization and supporting literatures five different biomasses are identified from the group for subsequent studies.

3.2 CHARACTERIZATION OF BIOMASS FEEDSTOCK

The fifteen different biomasses collected for characterization are (1) rice husk (2) bamboo dust (3) sugarcane bagasse (4) rice straw (5) newspaper (6) banana green leaves (7) switch grass (8) gulmohar leaves (9) falling dry leaves (10) elephant grass (11) saw dust (12) dry banana leaves (13) banana peel (14) banana pulp and (15) tea-waste. These biomasses are identified based on the supporting data from the literature as well as their abundance in the North Eastern Region of India.

The characterization of the above mentioned lignocellulosic biomass is carried out by performing proximate as well as ultimate analysis. Determination of chemical oxygen demand, calorific value of the biomass is also performed on the biomass to check their potentiality for biogas production. Since literature on biogas production from most of these lignocellulosic biomass are hardly found, biogas production from fresh cattle dung is also examined to compare the results with that of the lignocellulosic biomasses. The characterization of the biomass includes the determination of the following parameter.

1. Moisture content
2. Volatile Matter content
3. Ash content
4. Total Solid content

→ Determined by ASTM Method of proximate analysis

5. Lignin
6. Cellulose
7. Hemicellulose

→ Determined by Fibre Estimation Equipment following Van Soest Method

8. pH → Determined by pH meter
9. Elemental analysis → Determined by EDX SEM analysis
10. Chemical Oxygen Demand) → Determined by open reflux method by APHA

The proximate and ultimate analysis of the above mentioned biomasses are carried out as per the standard method described below.

3.2.1 PROXIMATE ANALYSIS

3.2.1.1 MOISTURE CONTENT

The moisture content of the feed material is determined as follows: approximately 2 g of the sample biomasses are weighed in a pre-weighed porcelain crucible using an electronic balance with least count of 0.001 g. The samples are placed in the drying oven at 105±3°C for

3 hours. After cooling the samples to room temperature in desiccators, final weight of the dried samples with pre-weighed crucibles are recorded. The percentage of moisture content of the sample biomasses are then calculated by using the following relation.

$$\%M = \frac{W_w - W_d}{W_w} \times 100\% \tag{3.1}$$

where

%M= moisture content in % (wet basis)

W_w= weight of the wet sample in g

W_d= weight of the oven dried sample in g

3.2.1.2 VOLATILE MATTER CONTENT

Volatile matter content is determined following standard test methods E872-82 (Reapproved 2006). Approximately 1 g of the oven dried sample used for determination of moisture content are further dried at 950±20°C and allowed to ignite for 7 minutes in pre-weighed porcelain crucible with lid. After cooling the samples to room temperature in desiccator, final weight of the cooled crucibles with lid containing the remaining of the burnt sample are recorded. The volatile solid content of the samples is calculated using Eq. 3.2 and 3.3.

$$\text{Weight loss } \% = \frac{W_i - W_f}{W_i - W_c} \times 100 = A \tag{3.2}$$

where

W_c = weight of crucible and cover in g

W_i = initial weight in g

W_f = final weight in g

$$\text{Volatile matter, } \% = A - B \tag{3.3}$$

where

A = weight loss, %

B = moisture, %

3.2.1.3 ASH CONTENT

Approximately 1 g of the oven dried sample used for determination of moisture content are further dried at 575±25°C and allowed to ignite completely for 3 hours in pre-weighed porcelain crucible. After cooling the samples to room temperature in desiccator, final weight

of the cooled crucibles containing the remaining of the burnt samples are recorded. The ash content of the samples is calculated using Eq. 3.4.

$$\%ash = \frac{\left(m_{as} - m_{cont}\right)}{\left(m_{od} - m_{cont}\right)} \times 100\% \tag{3.4}$$

where

% ash = mass percent of ash, based on 105°C oven-dried mass of the sample

m_{ash} = mass of ash and container in g

m_{cont} = tare mass of container in g

m_{od} = initial mass of 105°C dried sample and container

3.2.1.4 TOTAL SOLID (TS) CONTENT

TS content of feed materials are determined by following standard test methods ASTM E1756-08. Nearly 2 g of the sample biomasses are weighed in a pre-weighed porcelain crucible using an electronic balance with least count of 0.001 g. The samples are placed in the drying oven at 105±3°C for 3 hours. After cooling the samples to room temperature in desiccator, final weight of the dried samples with pre-weighed crucibles are recorded. The percentage of TS content of the sample biomasses are then calculated by using Eq. 3.5.

$$\%T_{105} = \frac{\left(m_{f1} - m_t\right)}{\left(m_{i1} - m_t\right)} \times 100\% \tag{3.5}$$

where

$\%T_{105}$ = mass percent of TS based on 105°C dry mass

m_t= tare mass of dried container

m_{i1} = initial mass of container and biomass

m_{f1} = final mass of container and biomass after drying at 105°C

3.2.1.5 FIXED CARBON CONTENT

The fixed carbon is a calculated value. It is the resultant of the summation of percentage moisture, ash and volatile matter subtracted from 100. All percentages shall be on the same moisture reference base.

$$\text{Fixed carbon \%} = 100 - (\text{M\%} + \text{ash\%} + \text{volatile matter \%}) \tag{3.6}$$

3.2.2 ULTIMATE ANALYSIS

The ultimate analysis determines the weight percentage of elements present in biomass like carbon, hydrogen, nitrogen, oxygen and sulphur. This analysis is conducted on the sample to determine its chemical composition at a particular point by EDXA using Scanning Electron Microscope (SEM), LEO 1430VP, [Zeiss, Germany] with an attachment of energy dispersive X-ray (EDX) system (Make: Oxford, UK). The instrument works on the principle of thermal conductivity detector (TCD).

3.2.3 CHEMICAL OXYGEN DEMAND (COD)

COD is a measure of the capacity of biomass to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals present in it. COD values of different samples have been determined by the modified open reflux method [Yadvika et al., 2006], which are suitable for samples with high percentages of suspended solids. COD assays are conducted according to open reflux method. 50 ml water and concentration of dry solid sample (in the form of chip) is taken in a round bottom flask along with a pinch of $HgSO_4$ and 20 ml $K_2Cr_2O_7$ solution. The contents are then placed in on a heating mantle. Then 60 ml H_2SO_4 solution is added from open end of a straight tube condenser through which cold water is circulated so that condensate fall back into the flask. The mixture is heated to boiling temperature. After the required refluxing time is over, the heating mantle is switched off and round bottom flask is left to cool at room temperature. After cooling, the condenser is washed with 50 ml distilled water and the round bottom flask is removed from the heating mantle. Mixture is titrated against standard ferrous ammonium sulphate (FAS) solution using ferroin indicator. COD in mg/l of original slurry sample is calculated as follows using Eq. 3.7 and 3.8.

$$COD(mg/l) = \frac{(\text{A-B}) \times \text{M} \times 8000}{\text{V}} \qquad (3.7)$$

where

A is volume of blank titrant (ml)

B is volume of sample titrant (ml)

M is the molarity of FAS solution= $\frac{\text{Volume 0.04167M } K_2Cr_2O_7 \text{ solution titrated, ml}}{\text{Volume FAS used in titration, ml}} \times 0.2500$

$$V = \frac{X_1}{X} \times Y \tag{3.8}$$

where

Y = the mass of the dry solid sample used for analysis

X_1 = the volume of the original slurry sample used for drying

X = solid content of X_1 ml of the slurry sample

V = the volume in ml of original slurry, which would have contained Y grams of dry solids

3.2.4 CALORIFIC VALUE OF FEED MATERIALS

The calorific value of feed material is the amount of heat liberated when unit mass of fuel get completely burnt under the atmosphere of excess oxygen. It is expressed in MJ/kg. Calorific value of biomass is determined using isothermal bomb calorimeter. The biomass sample is placed in a totally enclosed vessel and is burnt at a constant volume in presence of excess oxygen by igniting electrically. The water equivalent of the bomb calorimeter is determined by burning a known amount of benzoic acid and the heat liberated during the combustion process is absorbed by a known amount of water. The calorific value of the sample is calculated using Eq. 3.9.

$$C_v = \frac{W_c \times \Delta T}{M_s} \tag{3.9}$$

where

C_v = Heat of combustion of the biomass sample, MJ/kg

W_c = Water equivalent of the bomb calorimeter, MJ/$^\circ$C

$W_c = 10.74 \times 10^{-3}$ MJ/$^\circ$C

=2568.293 cal/$^\circ$C

ΔT = Rise in temperature, $^\circ$C

M_s = Mass of the biomass sample burnt, kg.

3.2.5 FIBRE ANALYSES OF BIOMASS

The fibre content of lignocellulosic biomass such as cellulose, hemicellulose and lignin can be determined by the analysis of the neutral detergent fibre (NDF), acid detergent fibre (ADF) and acid detergent lignin(ADL) using the reflux apparatus (Goering, et al. 1970). NDF is usually used to estimate the total lignocellulosic materials (including cellulose, hemicellulose and lignin), while ADF is used to estimate the content of lignin and cellulose. Hemicellulose content can be determined by the percentage difference between NDF and ADF. Cellulose content can be determined by the percentage difference between NDF and ADL.

3.3 SAMPLE PREPARATION

The biomasses are collected from the North Eastern Region of India and cleaned. For proximate analysis sugarcane bagasse, rice straw, newspaper, banana green leaves, switch grass, falling dry leaves, elephant grass and dry banana leaves are chopped to make 2 to 3 mm in length. All the biomasses are dried in the hot air oven for 24 hours and separately ball milled. After that they were strained through IS sieves of size 18. The undersized particles were used as feed material sample for ultimate analysis, determination of calorific value and COD.

3.4 RESULTS AND DISCUSSION

3.4.1 PROXIMATE ANALYSIS

The characterization study is carried out on fifteen different types of lignocellulosic biomass viz. rice husk, bamboo dust, sugarcane bagasse, rice straw, newspaper, banana green leaves, switch grass, gulmohar leaves, falling dry leaves, elephant grass, saw dust, dry banana leaves, banana peel, banana pulp and tea-waste. Characterization of fresh cattle dung is also carried out. Fresh material of the samples are tested in triplicate for proximate analysis which gives the moisture content, volatile matter content, ash and total solid as they are the main indicator to estimate the potentiality of their biogas production. The physiochemical properties of the feed material obtained from the proximate analysis of the biomass samples are discussed below. The moisture content of biomass is expressed as the amount of water per unit mass of dry biomass. It affects the heating value of the biomass. High moisture content of biomasses indicates low heating value since heat is necessary to evaporate the moisture contained. Fig. 3.2 shows the bar diagram of the results of moisture content of the biomasses.

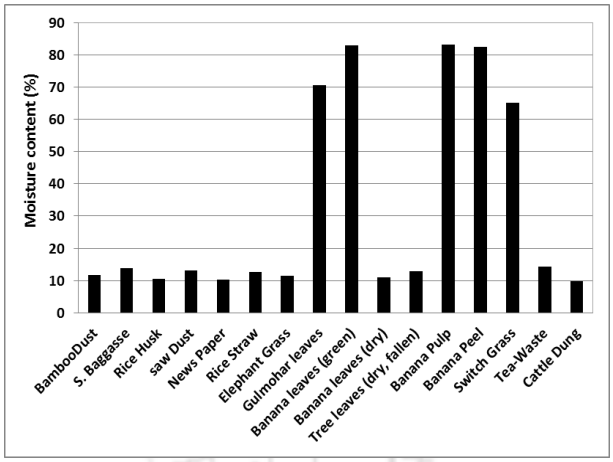


Fig. 3.2 Moisture content of biomass

It is observed that for rice husk, bamboo dust, sugarcane bagasse, rice straw, newspaper, falling dry leaves, elephant grass, saw dust and dry banana leaves moisture content ranged from 10-15%. Whereas for gulmohar leaves, banana green leaves, banana pulp, banana peel, switch grass and fresh cattle dung moisture percentage varied from 65–82%.

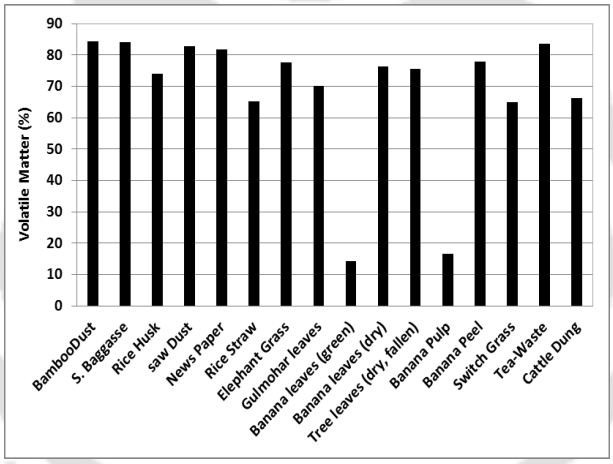


Fig. 3.3 Volatile matter content of biomass

Fig. 3.3 shows the volatile matter content in the lignocellulosic biomasses. It is observed that volatile matter content of the biomasses are quite good and it ranged from 56-74% which is comparable with literature [Miskam et al., 2009]. Whereas for gulmohar leaves volatile matter content is 28%, for banana green leaves 15%, for banana pulp and switch grass it is 16%. High volatile matter content indicates good potential for biogas production. The consequence of the volatile matter and fixed carbon is that they are responsible for how easily the biomass can be dissolved.

The ash content of biomass is the non-volatile inorganic matter which remains after subjecting it to a high decomposition temperature 500°C-550°C. Lower the ash content better

the biomass fuel is. It is observed from Fig. 3.4 that rice straw has got very high ash content (20%), followed by rice husk (15%). Elephant grass and banana leaves (dry as well as green) contain ash content approximately 13-14%. News paper, fresh cattle dung, dry leaves and switch grass contain approximately 7-9% ash content. Rest of the biomasses viz. bamboo dust, sugarcane bagasse, saw dust, gulmohar leaves, banana pulp and banana peel contain less than 5% ash content. Ash content of sundried cattle dung is found to be 22% whereas the same for fresh cattle dung is 9.55%.

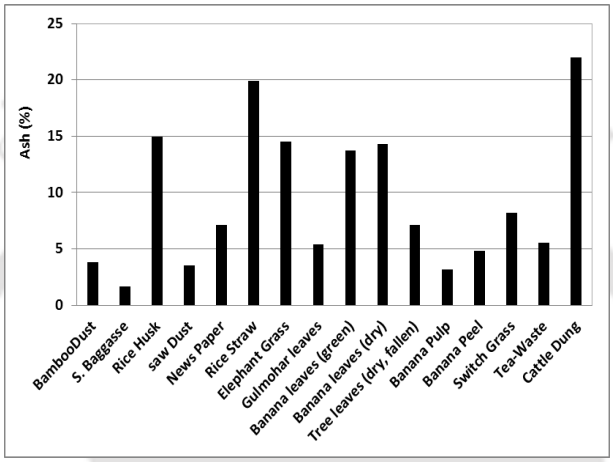


Fig. 3.4 Ash content of biomass

Total solid is an important parameter for biogas production. Hills and Roberts, 1981 reported that in case of cattle dung, best biogas yield was obtained when total solid is 8%. Budiyono et al., 2010 stated that TS content of 7.4 and 9.2% in cattle dung exhibit the best performance for digestibility. TS mainly consist of organic and inorganic matter present in biogas.

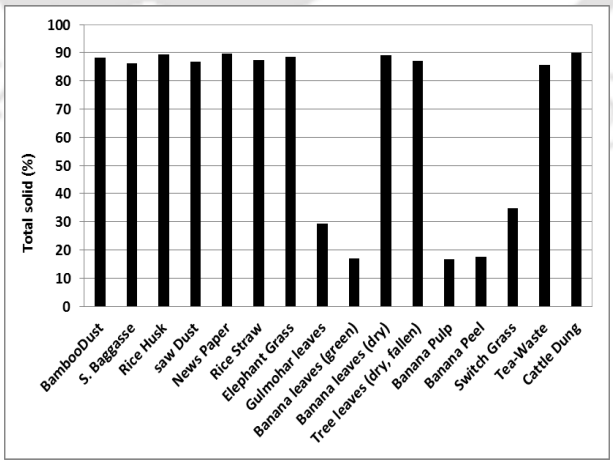


Fig. 3.5 Total solid content of biomass

Fig. 3.5 shows the TS content of the biomasses. From the analysis it is found that TS of rice husk, bamboo dust, sugarcane bagasse, rice straw, newspaper, falling dry leaves, elephant

grass, saw dust, dry banana leaves, cattle dung (sundried) and tea-waste ranges from 85-90%. Whereas for Gulmohar leaves and switch grass it ranges from 29-34% and for banana pulp and banana green leaves it ranges from 16-17%.

Fixed carbon content of biomass is shown in Fig. 3.6. It is observed that fixed carbon content of rice husk, bamboo dust, sugarcane bagasse, rice straw, newspaper, banana green leaves, falling dry leaves, elephant grass and banana pulp fall in the range of 10-15%, whereas in case of switch grass, gulmohar leaves and saw dust fixed carbon varies ranges from 19-26% and in case of dry banana leaves and tea-waste fixed carbon is approximately 6-7%. High fixed carbon indicates good potential for biogas production.

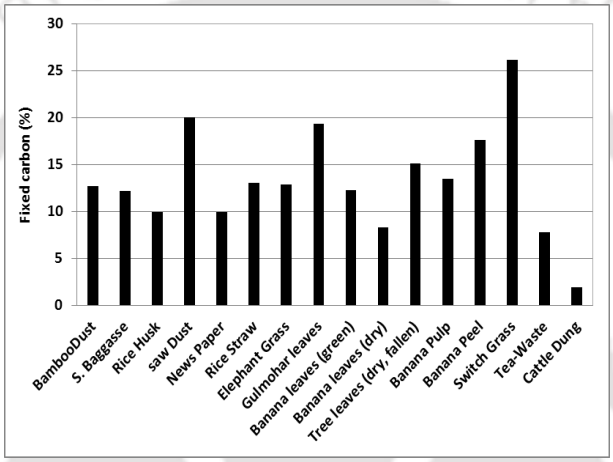


Fig. 3.6 Fixed carbon content of biomass

Table 3.1 shows the comparison of proximate analysis data of the above mentioned feed material along with the available literature data. It is observed that the data obtained from the proximate analysis of the feed material in the present work is quite comparable with the most of the available literature.

Table 3.1 Comparison of results of proximate analysis of the feed material and literature

Biomass type	Present work			LHV (MJ/kg	Literature data				LHV (MJ/kg)	Literature
	FC	ASH	VM		FC	ASH	VM	M		
Bamboo Dust	12.70	3.79	84.24	16.75	--	1.2	--	--	--	Buragohain B. et al., 2011
					9.3	16.5	74.2			Parikh et al., 2005
News Paper	9.93	7.10	81.81	11.72	--	--	--	--	--	
Cattle Dung	21.45	12.35	66.2	14.676	19.3	19.3	46.4	15	11.4	Roy et al., 2010

Table 3.1 (**Contd..)** Comparison of results of proximate analysis of the feed material and literature

Biomass type	Present work			LHV (MJ/kg	Literature data				LHV (MJ/kg)	Literature
	FC	ASH	VM		FC	ASH	VM	M		
S. Baggasse	12.19	1.68	84.17	18.46	12.4	2.1	85.5	--	--	Miles et al., 1995
					15.8	2.9	84.2	--	--	Raveendran et al., 1995
					13.15	3.2	83.66			Yin C.Y., 2011
Rice Husk	9.93	14.98	74.06	14.27	19.2	18	62.8	--	--	Miles et al., 1995
					13.1	0.8	73.8	12.3	13.36	Ve´ lez et al., 2009
					18.4	23.5	81.6	--	--	Raveendran et al., 1995
					16.95	21.24	61.81			Channiwala and Parikh, 2002
Saw Dust	19.98	3.51	82.79	14.33	14.3	1.1	84.6	--	--	Tillman, 2000
					14.04	1.49	76.23	--	--	Miskam et al., 2009
Rice Straw	13.03	19.93	65.15	13.73	15.6	20.1	64.3	--	--	Miles et al., 1995
					16.55	12.64	65.23	5.58	14.40	Li et al., 2009
					13.91	20.38	65.7			Channiwala and Parikh, 2002
Elephant Grass	12.861	14.489	77.550	17.699	--	--	--	--	--	
Gulmohar leaves	19.352	5.380	28.888	23.602	--	--	--	--	--	
Banana leaves (green)	12.261	13.730	14.364	14.898	--	3.10	22.2	--	--	Sellin et al., 2010
Banana leaves (dry)	8.270	14.326	76.383	16.694	--	7.5	77.8	--	--	Sellin et al., 2010
Dry tree leaves	15.111	7.153	75.512	21.438	--	--	--	--	--	
Banana Pulp	13.466	3.188	16.528	15.227	--	--	--	--	--	
Banana Peel	17.620	4.800	78.000	16.128	--	--	--	--	--	
Switch Grass	26.139	8.226	16.730	15.027	14.5	5.1	80.4	--	--	Miles et al., 1995
					14.34	8.97	76.69	--	--	Yin CY, 2011
Tea Waste	7.768	5.539	83.645	16.875	13.6	1.4	85	--	--	Parikh et al., 2005

3.4.2 ULTIMATE ANALYSIS

Ultimate analysis of biomass is done to assess the chemical composition of the biomass. Table 3.2 presents the comparisons of ultimate analysis data of the above mentioned lignocellulosic biomass obtained from the present work as well as literature. It is observed from the table that in case of bamboo dust, sugarcane bagasse, rice husk, rice straw, cattle dung and switch grass, carbon content obtained from the present work is comparable with the literature data. Whereas in case of banana leaves (dry as well as green) and saw dust the carbon content is almost 20% higher in present work than that of literature data. In case of tea waste and banana peel, carbon content is lower in present work than that of literature data. The difference in results of present work and literature may be due to the different working environment of chemical analysis. On the other hand, in case of elephant grass, gulmohar leaves, dry tree leaves, banana pulp and news paper result of ultimate analysis is hardly found in literature. Nitrogen content of all the biomasses in present work is found to be comparable with the available literature data.

Table 3.2 Comparison of results of ultimate analysis of the feed material and literature

Substrate	**Present study**				**Literature value**				
Feed Material	C (%)	N (%)	O (%)	Si (%)	C (%)	H (%)	N (%)	O (%)	Literature
Bamboo Dust	49.79	0.99	--	--	39.88	5.5	0.89	47.92	Buragohain B. et al., 2011
S. Baggasse	50.39	0.83	48.78	--	43.8	5.8	0.4	47.1	Kirubakaran et al., 2009
					49.8	6.0	0.2	43.9	Miles et al., 1995
Rice Husk	32.79	0.355	39.75	--	38.9	5.1	0.6	32.0	Kirubakaran et al., 2009
					49.3	6.1	0.8	43.7	Miles et al., 1995
Rice Straw	32.19	0.984	--	--	36.9	5.0	0.4	37.9	Kirubakaran et al., 2009
					50.1	5.7	1.0	43	Miles et al., 1995

Table 3.2 (**Contd..)** Comparison of results of ultimate analysis of the feed material and literature

Substrate	**Present study**				**Literature value**				
Feed Material	C (%)	N (%)	O (%)	Si (%)	C (%)	H (%)	N (%)	O (%)	Literature
Cattle Dung	35	1.6	55.42	0.01	33.33	--	1.68	--	Raheman and Mondal, 2012
					31.6	5.18	6.12	37.8	Roy et al., 2010
Elephant Grass	50.87	0.84	32.39	15.9	--	--	--	--	--
Gulmohar leaves	45	4.33	--	--	--	--	--	--	--
Banana leaves(green)	17.67	0.81	38.02	0.52	15.9	9.21	1.39	73.4	Sellin et al., 2010
Banana leaves (dry)	45.02	1.65	26.83	6.41	43.5	6.28	1.31	48.7	Sellin et al., 2010
Tree leaves (dry, fallen)	44.4	1.7	25.7	3.20	--	--	--	--	--
Banana peel	10.82	1.85	37.39	1.49	41.37	--	1.06	--	Bardiya et al., 1996
Banana Pulp	23.92	1.28	72.96	0.15	--	--	--	--	--
Switch Grass	46.41	1.08	36.38	13.37	46.7	5.9	0.8	37.4	Demirbas A., 2004
					49.7	6.1	0.7	43.4	Miles et al., 1995
Tea-Waste	26.57	0.8	65.59	0.22	48.0	5.5	0.5	44.0	Demirbas A., 2004
Saw Dust	50.37	0.77	36.05		42.38	5.27	0.14	42.41	Miskam et al., 2009
News Paper	41.82	0.84	46.68	2.29	--	--	--	--	--

3.4.3 CALORIFIC VALUE OF BIOMASS

From Fig. 3.7 it is observed that calorific value of the above mentioned lignocellulosic biomasses are quite good, which ranges from 12 to 22 MJ/kg. It is found to be the highest in case of dry tree leaves (22 MJ/kg). Rest of the biomass has calorific value in the range of 12-18 MJ/kg.

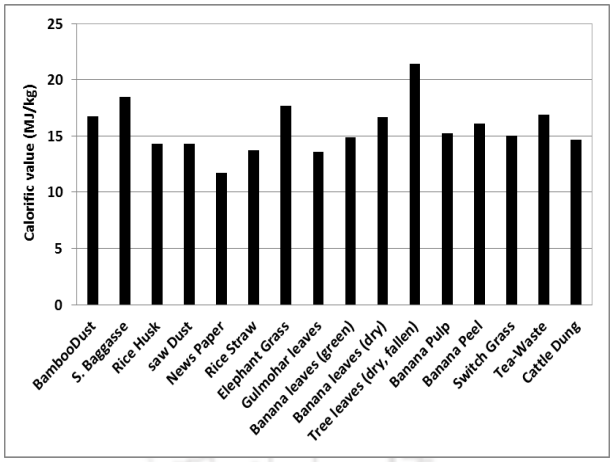


Fig. 3.7 Calorific value of biomass

3.4.4 CHEMICAL OXYGEN DEMAND OF BIOMASS

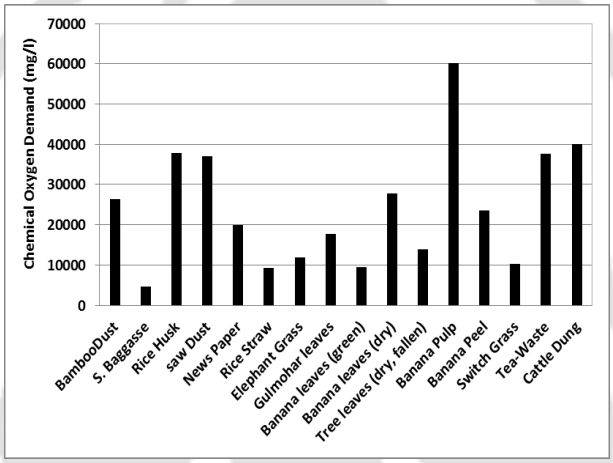


Fig. 3.8 Chemical oxygen demand of biomass

The above mentioned biomasses have a wide range of chemical oxygen demand as shown in Fig. 3.8. Banana pulp has the highest COD (60000 mg/L). Rice husk, saw dust and tea waste have approximately 37000-38000 mg/L COD. Bamboo dust, dry banana leaves and banana peel has COD value of 22000-26000 mg/L, whereas rest of the biomass have less than 20000 mg/L COD value. Cattle dung has got COD of 40020.21 mg/l which is comparable with literature data [Yadvika et al., 2006].

3.4.5 FIBRE ANALYSIS

Fiber analysis of lignocellulosic biomass such as elephant grass, rice straw, news paper, rice husk, saw dust, bamboo dust, sugarcane bagasse, switch grass, dry fallen leaves, banana peel, tea waste and fresh cattle dung been has been done so far. Figure 3.9-3.11 presents the results of fibre analysis which reveals the lignin to cellulose ratio along with the other

polymers namely cellulose, hemicellulose and lignin content of the above mentioned biomass.

Figure 3.9 shows the cellulose content of the above mentioned biomass. It is observed that cellulose content of the above mentioned lignocellulosic biomasses is quite good. Higher cellulose content indicates good potential for biomethanation. Among them, banana peel has got highest cellulose content (58%) followed by saw dust, bamboo dust, dry fallen leaves, News paper and sugarcane bagasse and rest of the biomasses have got 25-32% cellulose content.

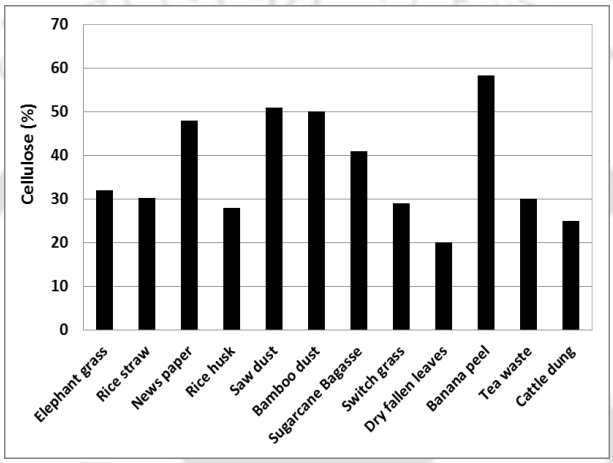


Fig. 3.9 Cellulose content (%) of biomass

Fig. 3.10 shows the hemicellulose content of lignocellulosic biomass. It is seen that except saw dust and bamboo dust all of the biomass has got high value of hemicellulose content. Among them switch grass has got highest amount of hemicellulose (45%).

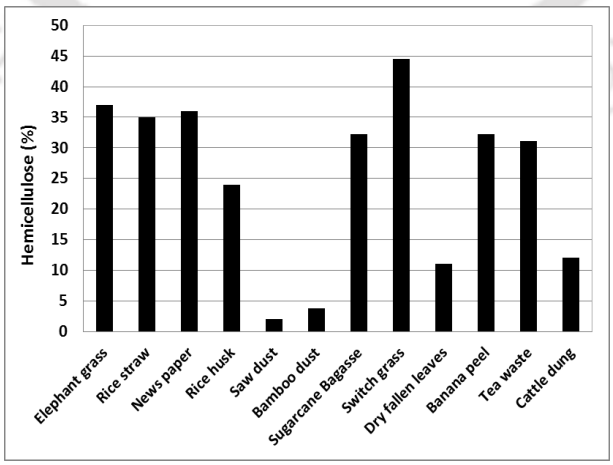


Fig. 3.10 Hemicellulose content (%) of biomass

Elephant grass, rice straw, news paper, sugarcane bagasse, banana peel and tea waste has hemicellulose content in the range of 31-37%. Rice husk, dry tree leaves and cattle dung has got 24%, 18% and 12% hemicellulose content respectively. Saw dust and bamboo dust has got less than 5% hemicellulose content.

Fig. 3.11 shows the lignin content (%) of the above mentioned biomass. It indicates that the higher the lignin content lower is the digestibility of the biomass as it is difficult to degrade in anaerobic condition. It binds the cellulose and hemicellulose content in an intense cross link. Hence it is necessary to break the lignin before using the biomass for fermentation or biomethanation. It is observed from the Fig. 3.11 that rice straw, news paper, rice husk, saw dust, tea waste are having a considerable amount of lignin (> 20%). Whereas for sugarcane bagasse, switch grass and banana peel, lignin content varies from 12-18%. Elephant grass, bamboo dust, dry tree leaves and cattle dung has got very little lignin content in the range of 3-8%.

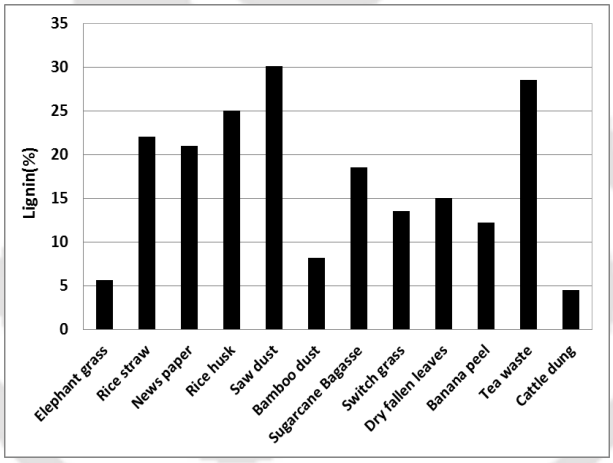


Fig. 3.11 Lignin content (%) of biomass

Lignocellulosic biomass gives a unique and sustainable resource for environmentally safe organic fuels and chemicals. However, the digestibility of lignocellulosic biomass is low owing to structural features such as lignin content, crystallinity etc. In case of lignocellulosic biomass the lignin to cellulose ratio is normally used to define the degree of digestibility of the biomasses [Sharma, 1988]. From the Fig. 3.12 it is observed that lignin to cellulose ratio is the highest in case of rice husk (0.892) followed by rice straw (0.7284), saw dust (0.590), sugarcane bagasse (0.451) and bamboo dust (0.164) respectively.

The sample calculation for the characterization of biomass is shown in Appendix I.

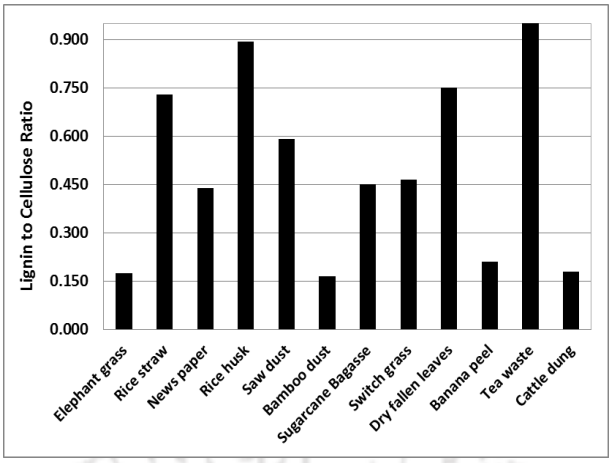


Fig. 3.12 Lignin to cellulose ratio (%) of biomass

3.5 SELECTION OF LIGNOCELLULOSIC BIOMASS FOR PRESENT STUDY

Based on the results of characterization of the above mentioned feed material a selection criteria was made, according to which five best feed materials were selected for carrying out the biomethanation process. The selection criteria was based on the fact that the chosen feed material should have good volatile matter and carbon content, high calorific value, less ash content and acceptable percentage of cellulose content. The five feed material selected for carrying out biomethanation was bamboo dust, saw dust, sugarcane bagasse, rice straw and rice husk. All of them have more than 60% volatile matter content, more than 10% fixed carbon content, more than 14 MJ/kg calorific value and more than 30% cellulose content which make them good potential for biogas production. Ash content of bamboo dust, saw dust and sugarcane bagasse are less than 5%, whereas rice husk and rice straw have approximately 15% and 20% ash content. Since lignin content of these biomasses except bamboo dust are also quite high, that is why physical pretreatment of these biomasses are carried out using ball milling to reduce the particle size which eventually helps in increasing their digestibility.

3.6 SUMMARY

In this chapter, characterization of the lignocellulosic biomass is carried out by performing proximate analysis, ultimate analysis, determining the chemical oxygen demand, calorific value and by estimating the fibre composition of the biomass. It is observed from the results that lignocellulosic biomass have very high amount of volatile matter content, carbon content and high calorific value which make them potential source of renewable energy. On the other hand most of the biomass have very high amount of lignin content too which resist the

decomposition of cellulose content of the biomass. As a result the fermentation of lignocellulosic biomass takes long period of time as compared to other non-lignocellulosic biomass. To avoid the delay in hydrolysis process of fermentation, pretreatment of biomass is done. Pretreatment of biomass breaks the lignin part of the biomass beforehand thus exposing the cellulose part of the biomass which makes it easier for the bacteria to decompose the biomass effectively thus avoiding delay in hydrolysis process. Subsequently, chapter 4 presents the effect of particle size of biomass, total solid of substrate, temperature of substrate and addition of biochar to biomass on biogas production from selected lignocellulosic biomasses.

CHAPTER 4

PARAMETRIC STUDY OF BIOGAS PRODUCTION

4.1 INTRODUCTION

This chapter presents the parametric study of biomethanation from selected lignocellulosic biomass co-digested with cattle dung in batch mode. Effect of particle size, total solid (TS), agitation, addition of biochar and digester temperature on biogas production are studied.The feed materials used in this research are bamboo dust, sugarcane bagasse, saw dust, rice straw and rice husk which are selected based on characterization done as discussed in chapter 3.

Anaerobic digestion is a process in which microorganisms degrade the biodegradable part of the organic material in the absence of oxygen to produce biogas mainly consists of methane and carbon dioxide. It mainly take place either at mesophilic (25°C-40°C) or thermophilic temperatures (45°C-60°C) [Usman et. al, 2012]. From literature survey it is seen that the effect of temperature on anaerobic digestion is significant beyond 45°C [Feilden, 1981; Henze and Harremoes, 1983; Rintala and Lettinga, 1992; Speece and Kern, 1970; Van Lier et al., 1990, Liar, 1995]. But most of the anaerobic digestion at thermophilic condition is studied mainly on cattle manure. Very few literature is available on effect of temperature (mesophilic as well as thermophilic) on anaerobic digestion of lignocellulosic biomass such as bamboo dust, saw dust, sugarcane bagasse, rice husk powder etc., which are abundantly available in North Eastern Region of India. A few researchers had reported on biogas production at thermophilic condition with *Laminaria digitata* (seaweed), wastewater and food waste [Kim et al., 2006; Vanegas and Bartlett, 2013]. This study focuses on the utilization of lignocellulosic biomass for biogas production by anaerobic digestion in mesophilic as well as in thermophilic condition.

4.2 PREPARATION OF SUBSTRATES

Fifteen different kinds of lignocellulosic biomasses are collected from North Eastern Region of India. Based on the characterization done in terms of VS, FC, CV, ash and cellulose content, five biomasses, namely, bamboo dust, saw dust, sugarcane bagasse, rice husk powder and rice straw are chosen as feed material for the performance study.

The samples are cleaned and dried for 5 to 6 hour to remove the superficial moisture. Subsequently, all the samples are dried in the hot air oven for 24 hours and separately ball milled. Bamboo dust, saw dust and rice husk powder were strained through Indian Standard (IS) sieves of different sizes 44, 30 and 18. The undersized particles were used as feed material for the anaerobic digestion. Thus, the sieved particles used in the digesters were in the range of 0 to 0.355, 0.355 to 0.5 and 0.5 to 0.85 mm, respectively. For easy handling, the sieved particles were represented as 0.355 mm, 0.5 mm and 0.85 mm, respectively. On the other hand, after collecting rice straw and sugarcane bagasse, they were dried for almost a month. After drying they were chopped to make 2 to 3 mm in length and separately ball milled. Finally the rice straw and sugarcane bagasse become fibrous in appearance which is used for biogas generation.

Literature reveals that maximum biogas production can be achieved with C:N in the range of 25:1 to 30:1, [Hills and Roberts, 1981]. The C:N of the biomasses considered in the present study varies widely from 32:1 to 82:1 as shown in Table 4.1. In case of cattle dung same is observed to be 21.8:1. In order to control the C:N in permissible limit for production of biogas effectively, the biomass considered were mixed with cattle dung in the ratio of 1:1, 1:3, 3:1, 3:2, 2:3 and 4:1 ratio and tested for the carbon and nitrogen content using energy dispersive X-ray (EDX) system [Make: Oxford, UK] attached to Scanning Electron Microscope (SEM) [make: LEO 1430VP, Zeiss, Germany]. It was found that the mixing of biomass with cattle dung in 1:3 produces C:N of the mixture in the range of 25:1 to 30:1. A comparison of C:N for all the above mentioned biomasses, before and after mixing with cattle dung is shown in Table 4.1.

Reiterating, cattle dung was mixed with each biomass in 1:3 ratios for all the experiment so that the C:N ratio of the mixed substrate is controlled in the range of 25:1-30:1. The aforementioned feed material prepared is mixed with water so as to control the TS. The requirement of feed material and water to make the substrate is shown in Annexure IV. Water was added to the mixture in 1:2 (mass: mass) so as to make the TS 12%. Similarly, water was added in 1:3 and 1:5 ratio to make TS 9% and 6%, respectively.

Calculations regarding control of C:N ratio and TS of substrates is shown in Appendix II.

Table 4.1 C:N ratio of biomass before and after mixing with cattle dung

Sl. No.	Biomass	Carbon (%)	Nitrogen (%)	C:N	Biomass + Cattle Dung (1:3)	C:N
1	Bamboo Dust	49.79	0.99	50.29:1	Bamboo Dust cattle dung mixture	25.20:1-26.73:1
2	Saw Dust	50.37	0.77	65.41:1	Saw Dust cattle dung mixture	27.0:1-30.19:1
3	Rice Husk Powder	32.79	0.4	92.36:1	Rice Husk Powder cattle dung mixture	26.72:1-28.06:1
4	Sugarcane Bagasse	50.39	0.83	60.7:1	Sugarcane Bagasse cattle dung mixture	27.6:1-30.1:1
5	Rice Straw	32.19	0.9	32.71:1	Rice Straw cattle dung mixture	23.71:1-25.08:1
6	Pure cattle dung	35	1.6	21.87:1	-----	-----

Samples of the substrate prepared are also tested for the TS following standard test methods given in ASTM E1756-08. Table 4.2 presents the TS (% mass by mass) for different ratio of feed mixture prepared to amount of water added.

Table 4.2 TS (% mass by mass) for different ratio of feed mixture

Ratio of feed mixture		TS (%)
(BD+CD):Water	1:2	12.11
(SB+CD):Water		11.94
(RH+CD):Water		12.21
(SD+CD):Water		11.99
(RS+CD):Water		12.04

Table 4.2 (**Contd..**) TS for different ratio of feed mixture

Feed mixture		**TS (%)**
(BD+CD):Water	1:3	9.08
(SB+CD):Water		8.96
(RH+CD):Water		9.16
(SD+CD):Water		8.99
(RS+CD):Water		9.03
(BD+CD):Water	1:5	6.06
(SB+CD):Water		5.97
(RH+CD):Water		6.10
(SD+CD):Water		5.99
(RS+CD):Water		6.02

4.3 EXPERIMENTAL SET-UP

The schematic diagram of the experimental set-up for batch biomethanation study is shown in Fig. 4.1. It consists of a laboratory bio-digester made of borosilicate glass of capacity 1000 ml with air tight rubber cork fitted into its opening. Thermometer and copper tubes are fitted through the holes made in the rubber cork for measuring the substrate temperature and to provide a passage for the gas flow through the connecting tube. The other end of the connecting tube is passed through a 500 ml bottle containing brine solution. The brine solution is used in a 500 ml bottle to inhibit absorption of CO_2 by water. The amount of biogas produced is measured by water displacement method. The biogas produced in the bio-digester goes through the connecting pipe to the bottle containing brine solution. The pressure of the biogas produced causes displacement of the brine solution to a beaker connected and placed on the other side of the solution bottle as shown in figure. The amount of solution collected in the beaker represented the amount of biogas produced. A sampling port provided through the rubber cork (fitted with a valve) facilitates the collection of substrate time to time to test the TS, VS and pH, respectively.

The substrate prepared is filled into the digester upto 900 ml volume and 100 ml is kept free at the upper portion of the digester for biogas accumulation. The bio-digester is then sealed with the rubber cork along with the other accessories as mentioned above. Entire digester is then kept inside a water bath so as to regulate the temperature of substrate contained in it. Due measures are taken to make the set up leak proof.

Similar set ups are replicated to conduct 80 (eighty) sets of experiments for the parametric study. Details of experiments conducted and set ups used are given in Table 4.3. The Entire experiment is repeated twice under the same working condition and the data from each run having better results (higher biogas production) were considered for further analysis.

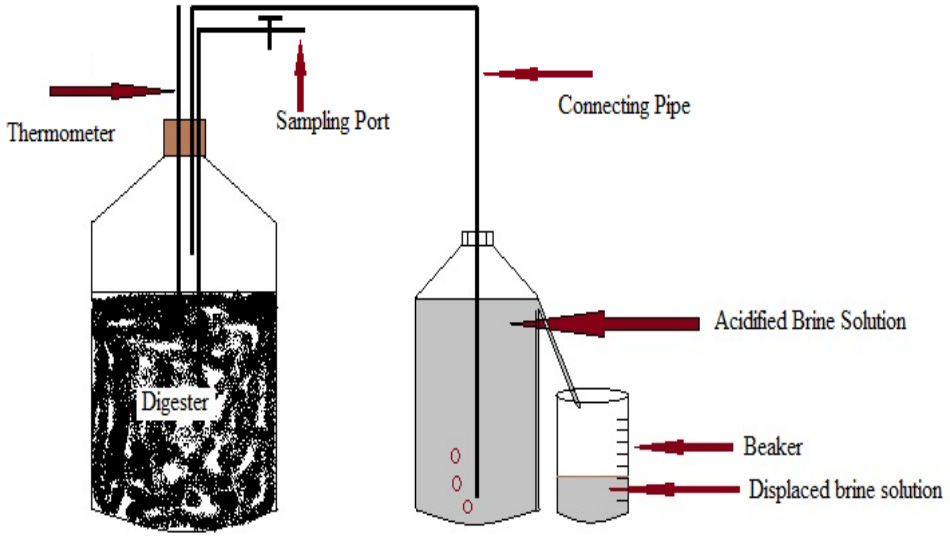


Fig. 4.1. Schematic diagram of experimental set-up

A weighing balance is used to measure the required mass of cattle dung and biomass. The mercury-in-glass thermometer (range -10°C to 110°C) fitted to the bio-digester through the cork is used to measure the daily temperature of the substrate and a digital pH meter is used to determine the pH of the fermented substrate. The digester is maintained at a constant temperature by putting it inside a water bath at a fixed temperature. The temperature of the substrate is measured twice a day with the help of the thermometer fitted through the cork. The biogas production is monitored daily and measured in an interval of every five days by means of water displacement method due to the fact that anaerobic digestion is a slow process. The biogas production is observed and recorded for 50 days. List of equipment used during the experiment is

given in Appendix III. The photograph of the water bath where the digesters are kept, the experimental set-up, weighing balance, digital pH meter, planetary ball mill and various accessories used in the experimental set-up are shown in Appendix IV.

Table 4.3 Details of experiments conducted on effect of various parameters at 50 days HRT

<table>
<tr><th rowspan="2">Feed Mixture</th><th colspan="4">Effect of Parameters</th></tr>
<tr><th>TS (mass by mass) at 35°C temperature</th><th>Particle size at 35°C temperature</th><th>Temperature (˚C) at 9% TS</th><th>Addition of biochar and agitation at 9% TS</th></tr>
<tr><td rowspan="12">BD+CD+Water</td><td rowspan="3">6%</td><td>0.85 mm</td><td rowspan="3"></td><td rowspan="12"></td></tr>
<tr><td>0.50 mm</td></tr>
<tr><td>0.355 mm</td></tr>
<tr><td rowspan="5">9%</td><td rowspan="2">0.85 mm</td><td>35</td></tr>
<tr><td>40</td></tr>
<tr><td rowspan="2">0.50 mm</td><td>45</td></tr>
<tr><td>50</td></tr>
<tr><td>0.355 mm</td><td>55</td></tr>
<tr><td rowspan="3">12%</td><td>0.85 mm</td><td rowspan="3"></td></tr>
<tr><td>0.50 mm</td></tr>
<tr><td>0.355 mm</td></tr>
<tr><td rowspan="8">SB+CD+Water</td><td>6%</td><td rowspan="3">Without milling</td><td rowspan="3"></td></tr>
<tr><td>9%</td></tr>
<tr><td>12%</td></tr>
<tr><td rowspan="2">6%</td><td rowspan="5">With milling</td><td>35</td></tr>
<tr><td rowspan="2">40</td></tr>
<tr><td rowspan="2">9%</td></tr>
<tr><td>45</td></tr>
<tr><td rowspan="2">12%</td><td>50</td></tr>
<tr><td>55</td></tr>
<tr><td rowspan="10">RH+CD+Water</td><td rowspan="3">6%</td><td>0.85 mm</td><td rowspan="3"></td></tr>
<tr><td>0.50 mm</td></tr>
<tr><td>0.355 mm</td></tr>
<tr><td rowspan="5">9%</td><td rowspan="2">0.85 mm</td><td>35</td></tr>
<tr><td>40</td></tr>
<tr><td>0.50 mm</td><td>45</td></tr>
<tr><td rowspan="2">0.355 mm</td><td>50</td></tr>
<tr><td>55</td></tr>
<tr><td rowspan="3">12%</td><td>0.85 mm</td><td rowspan="3"></td></tr>
<tr><td>0.50 mm</td></tr>
<tr><td>0.355 mm</td></tr>
</table>

Table 4.3 (**contd..)** Details of experiments conducted on effect of various parameters

<table>
<tr><th rowspan="2">Feed Mixture</th><th colspan="4">Effect of Parameters</th></tr>
<tr><th>TS (mass by mass) at 35°C temperature</th><th>Particle size at 35°C temperature</th><th>Temperature (˚C) at 9% TS</th><th colspan="2">Addition of biochar and agitation at 9% TS</th></tr>
<tr><td rowspan="9">SD+CD+Water</td><td rowspan="3">6%</td><td>0.85 mm</td><td rowspan="3"></td><td colspan="2" rowspan="15"></td></tr>
<tr><td>0.50 mm</td></tr>
<tr><td>0.355 mm</td></tr>
<tr><td rowspan="4">9%</td><td rowspan="2">0.85 mm</td><td>35</td></tr>
<tr><td>40</td></tr>
<tr><td rowspan="2">0.50 mm</td><td>45</td></tr>
<tr><td>50</td></tr>
<tr><td>0.355 mm</td><td>55</td></tr>
<tr><td rowspan="3">12%</td><td>0.85 mm</td><td rowspan="3"></td></tr>
<tr><td>0.50 mm</td></tr>
<tr><td>0.355 mm</td></tr>
<tr><td rowspan="6">RS+CD+Water</td><td>6%</td><td rowspan="3">Without milling</td><td rowspan="3"></td></tr>
<tr><td>9%</td></tr>
<tr><td>12%</td></tr>
<tr><td>6%</td><td rowspan="6">With milling</td><td>35</td></tr>
<tr><td rowspan="2">9%</td><td>40</td></tr>
<tr><td rowspan="2">45</td></tr>
<tr><td rowspan="3">12%</td></tr>
<tr><td>50</td></tr>
<tr><td>55</td></tr>
<tr><td rowspan="6">Cattle dung</td><td rowspan="2">6%</td><td rowspan="6"></td><td>35</td><td rowspan="2">2.5% of TS</td><td>Stirred</td></tr>
<tr><td rowspan="2">40</td><td>Non-stirred</td></tr>
<tr><td rowspan="2">9%</td><td rowspan="3">5% of TS</td><td>Stirred</td></tr>
<tr><td rowspan="2">45</td><td>Non-stirred</td></tr>
<tr><td rowspan="2">12%</td><td rowspan="2">50</td><td>Stirred</td></tr>
<tr><td>55</td><td rowspan="2">10% of TS</td><td>Non-stirred</td></tr>
<tr><td></td><td></td><td></td><td></td><td rowspan="2">No biochar</td><td>Stirred</td></tr>
<tr><td></td><td></td><td></td><td></td><td>Non-stirred</td></tr>
<tr><td>Total no. of digesters used</td><td colspan="2">42</td><td>30</td><td colspan="2">08</td></tr>
</table>

4.4 MATERIALS AND METHODS

Lignocellulosic biomass considered in the present study for biomethanation are bamboo dust, saw dust, sugarcane bagasse, rice straw and rice husk. The biomethanation of lignocellulosic biomass mixed with cattle dung as well as pure cattle dung is carried out in batch mode to investigate the effect of various parameters such as effect of total solid, particle size (pretreatment) and temperature on biogas production rate. Effect of agitation as well as addition of biochar to cattle dung on biogas production rate is also carried out.

4.5 PARAMETERS OF BIOMETHANATION STUDY

Table 4.4 shows the parameters of biomethanation process considered for batch reactors.

Table 4.4 Parameters of biomethanation study

Sl. No.	Parameters	Unit
1	Daily ambient and digestate temperature	°C
2	pH of feed-stock (at start and end of experiment)	
3	Daily Biogas production rate	ml/g VS/day
4	Composition of biogas (CH_4 and CO_2 content)	%
5	Cumulative biogas production for 50 days HRT	ml/g VS

4.5.1 AMBIENT AND DIGESTATE TEMPERATURE

The temperature affects the rate of reaction in biogas reduction. An increase in temperature generally increases the rate of reaction and therefore the rate of biogas production. A mercury-in-glass thermometer (range -10°C to 110°C) fitted to the bio-digester through the cork is used to measure the daily temperature of the substrate inside the digester. Another thermometer of same specification kept outside the digester is used to measure the ambient temperature. The constant temperatures of the digesters are maintained by putting the digesters in the water bath at fixed temperature.

4.5.2 pH

The pH of a solution is defined as the negative logarithm of its H^+ ion concentration i.e. pH = - log [H^+] or pH=log 1/[H^+]. It is a measure of substrate's acidity or alkalinity. A digester

operates well at a pH of 7.0 or above, i.e. slightly under alkaline conditions. The optimum pH range of the digester is 7 and 8.5 for increased gas yield [Mittal, 1996]. The methanogenic bacteria are very sensitive to pH changes and are active only in the narrow pH range (between 6.8 to 8.5) whereas the acidogenic bacteria can survive in as low a pH as 5.5 [Nijaguna, 2002]. A digital pH meter is used to determine the pH of the fermentation slurry. The pH meter is standardized using buffer of 4.0, 7.0 and 10.0 pH before measurement.

4.5.3 VOLUME OF BIOGAS PRODUCTION

The biogas production is observed and recorded for 50 days until biogas production reduces significantly. The daily volume of biogas produced during the entire batch biomethanation experiment is measured using water displacement system in the laboratory under ambient conditions. Brine solution is used in the water displacement method to avoid absorption of CO_2 by water during biogas measurement. It is prepared by adding NaCl to water until a supersaturated solution is formed. A few drops of concentrated sulphuric acid are added to the solution to make the brine solution acidic. The solution bottle containing brine solution is fitted to the batch reactors through connecting pipe. When biogas production takes place in the Bio-digesters, it is transferred to the solution bottle containing acidified brine solution through the connecting tube and applies pressure into the solution. As a result the solution come out through the outlet opening and gets poured into the measuring beaker. The amount of solution in the beaker indicates the amount of biogas production.

4.5.4 MEASUREMENT OF METHANE AND CARBON DI-OXIDE

The measurement of methane and carbon di-oxide contents in biogas was carried out in gas chromatograph (GC) analyser [model no. CHEMITO CERES 800 plus].

4.5.5 MEASUREMENT OF CUMULATIVE PRODUCTION OF BIOGAS

The cumulative production of biogas was calculated by adding daily biogas production yield.

4.6 RESULTS AND DISCUSSION

4.6.1 EFFECT OF AGITATION ON BIOGAS PRODUCTION

Effect of agitation on cumulative biogas production from cattle dung is presented in Fig. 4.2 considering HRT of 50 days. The experiment is conducted with and without agitation of

substrate. Agitation is done manually by shaking the digesters for 10-15 minutes twice in a day. It is observed from this figure that agitation enhances biogas production significantly. At HRT of 50 days the enhancement in biogas production is observed to be 69% in respect to non-agitated condition. This is due to the breaking of the scum formed with agitation at the top of the digester which gets the gas trapped inside the substrate. Also the dry matter of the feed stock get settle down at the bottom of the digester without agitation and gas production get hindered [Inthapanya et al., 2012]. The agitation facilitate the diffusion of the bacteria throughout the substrate and hence expose them homogenously to the undigested substrate [Karim and Hoffmann et al., 2005]. As a result most of the volatile solid content of feedstock gets used by the microorganisms resulting in better biogas production. Hence, subsequent experiments are conducted with manual agitation only.

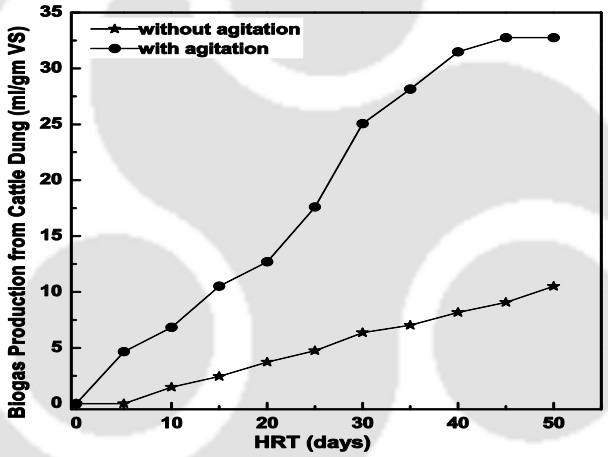


Fig. 4.2 Effect of agitation on biogas production from cattle dung

4.6.2 EFFECT OF PARTICLE SIZE AND TOTAL SOLID ON BIOGAS PRODUCTION

In the preliminary batch biomethanation the effect of particle size and total solid of feed-stock on biogas generation rate at a temperature of 35°C is carried out. In this part of investigation, the small scale laboratory experiments are carried out on above mentioned biomass with three different total solid concentrations. Three different particle sizes of 0.85, 0.5 and 0.355 mm are considered in case of bamboo dust, saw dust and rice husk powder, respectively. Pretreated and untreated rice straw and sugarcane bagasse are selected to study the effect of size reduction. The particle size reduction of bamboo dust, saw dust and rice husk powder is done by ball milling

and sieving with Indian Standard (IS) sieve of size 18, 30 and 44. The undersized particles of biomass are picked for the study.This phase of biomethanation study is carried out to optimize the suitable size of biomass particle and total solid of the substrate for maximum biogas generation.

The effect of TS of feedstock on biogas generation is carried out on cattle dung as shown in Fig. 4.3 and is observed that at 9% TS, cattle dung produces highest amount of biogas (1591 ml) followed by 12% (1199 ml) and 6% (993 ml) TS which is comparable with literature [Budiyono et al., 2010; Mahanta et al., 2004].

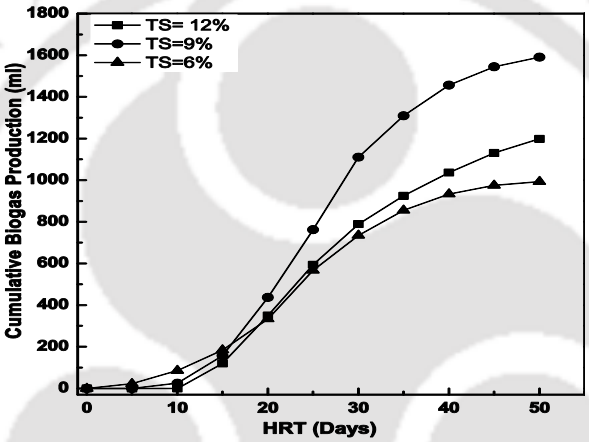


Fig. 4.3 Effect of total solid on biogas production from cattle dung

Figure 4.4 (a) shows the effect of particle size and TS on biogas generation from bamboo dust mixed with cattle dung. It is observed that highest biogas production was obtained with 9% TS and 0.355 mm particle size, followed by 9% TS and 0.5 mm particle size. Lowest amount of biogas was produced with 6% TS and 0.85 mm particle size. Similar is the case with saw dust and rice husk powder as shown in Fig. 4.4 (b) and (c), respectively, where highest amount of biogas was produced with 9% TS and 0.355 mm particle size and minimum gas production was obtained with 6% TS and 0.85 mm particle size. The results are comparable with that of cattle dung where highest biogas production is observed at 9% TS and lowest amount of biogas production was obtained at 6% TS of the substrate. Figure 4.4 (a) to (c) also reveals that difference in biogas production by biomass with particle size of 0.355 mm and 0.5 mm is only 80-160 ml at concentration of 9% TS. Hence to make the system economical biomass with 0.5 mm particle size can also be used for better production of biogas.

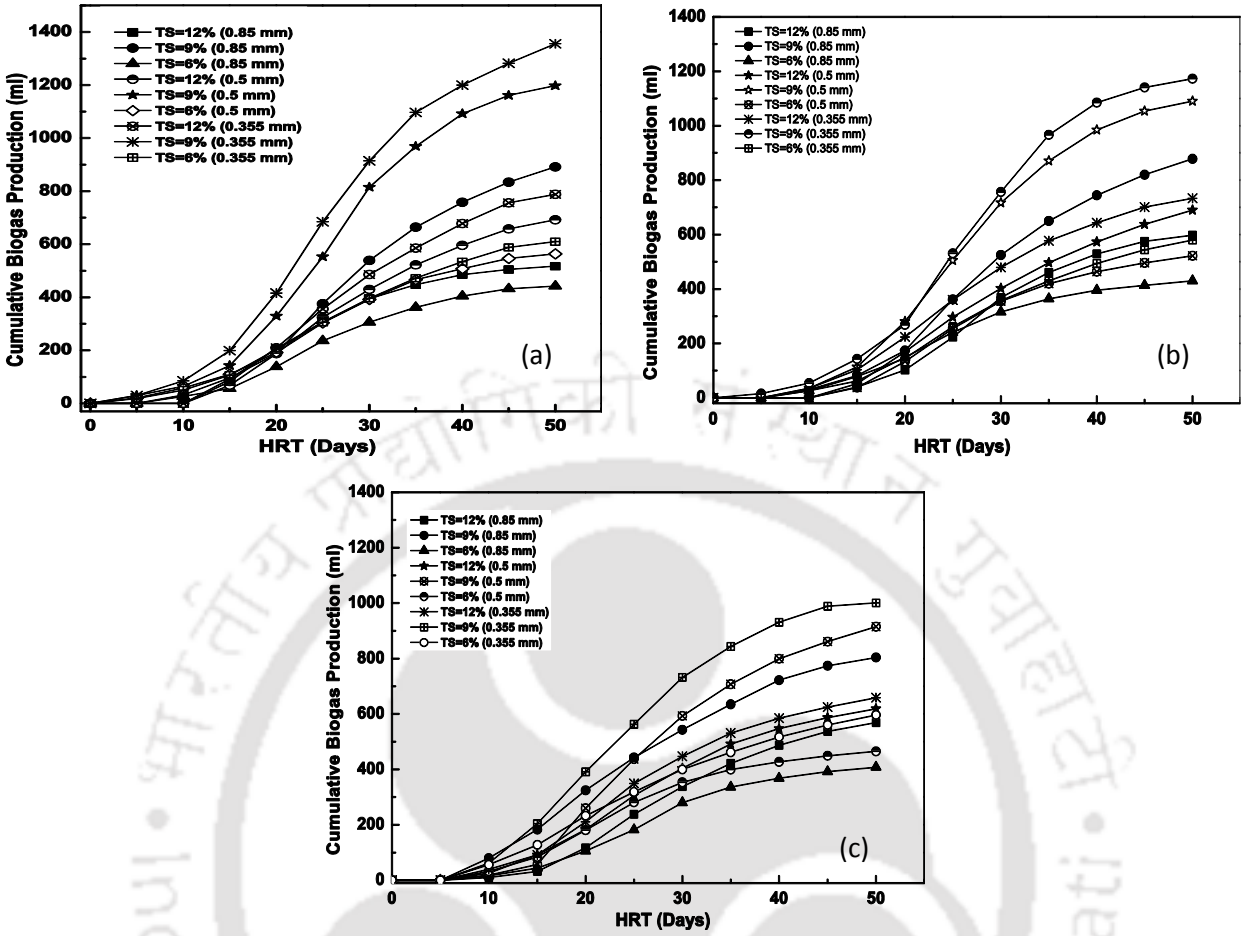


Fig. 4.4 Effect of particle size and total solid on biogas production from (a) bamboo dust, (b) saw dust and (c) rice husk powder mixed with cattle dung

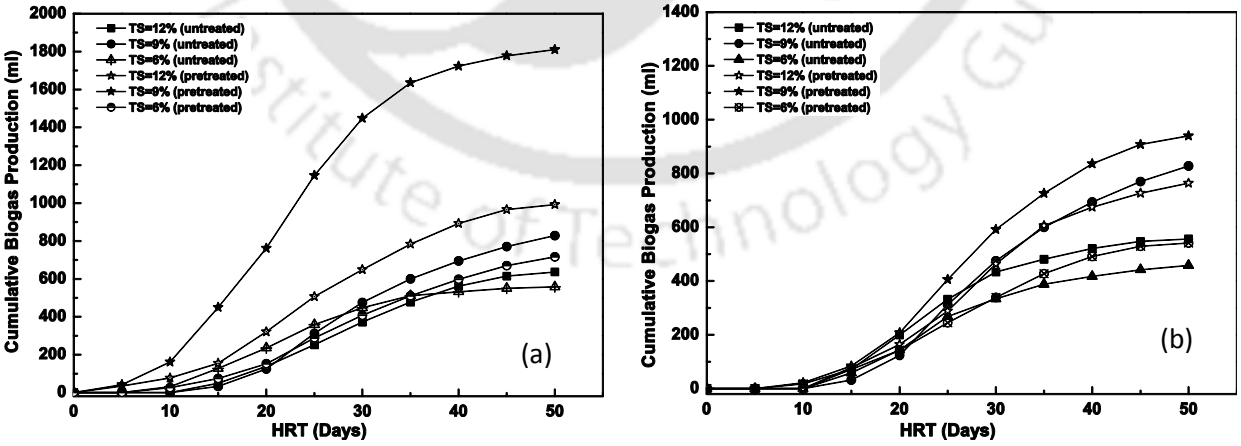


Fig. 4.5 Effect of total solid on biogas production from pretreated and untreated (a) sugarcane bagasse and (b) rice straw mixed with cattle dung.

Figure 4.5 (a) shows the effect of pretreated and untreated sugarcane bagasse with TS concentration of 6%, 9% and 12%, respectively. It is observed from the figure that at 9% TS the pretreated sugarcane bagasse mixed with cattle dung gives the highest biogas production followed by 12% TS with pretreated condition and untreated biomass at 9% TS produces higher biogas than that of pretreated biomass at 6% TS. Lowest biogas production was obtained at 6% TS in untreated condition. Similarly in case of rice straw mixed with cattle dung the highest biogas production was obtained at 9% TS in pretreated condition and lowest biogas production was obtained at 6% TS in untreated condition as shown in Fig. 4.5 (b).

The results suggest that TS content of substrate affects the biogas generation from biomass significantly. It was found that biomass with particle size of 0.355 mm mixed with cattle dung produced the highest amount of biogas followed by biomass with particle size of 0.5 mm and 0.85 mm, respectively at all the three TS concentrations. Also, biogas production from these biomasses with particle size of 0.355 mm mixed with cattle dung started earlier as compared to that with particle size of 0.85 mm mixed with cattle dung. This attribute to the fact that with size reduction of particle in biomass surface area increases exposing the cellulose content to the microorganisms which eventually leads to the early and better digestibility. Out of the three TS concentrations biogas production was found to be highest at 9% TS followed by 12% and 6% irrespective of particle size. In case of sugarcane bagasse and rice straw pretreated biomass with 9% TS produced highest amount of biogas and untreated biomass with 6% TS produced very insignificant amount of biogas in 50 days HRT.

Pretreated biomass shows better results as compared to untreated biomass. The reason is that with pretreatment particle size of biomass reduces thus breaking the lignin part of biomass and increasing the exposed area of biomass. As a result the cellulose content of biomass gets uncovered for microorganisms leading to decomposition which reduces the lignin to cellulose ratio. Consequently digestibility of biomass increases and production of biogas enhances.

4.6.3 EFFECT OF TEMPERATURE ON BIOGAS PRODUCTION

It is already established that the effectiveness of anaerobic digestion naturally depends upon the intensity of bacterial activity. Therefore it is very important to control the factors that affect the bacterial activity [Mittal, 1996]. Temperature is one important factor which affects the anaerobic

digestion. Anaerobic digestion can take place under psychrophilic (<15°C), mesophilic (15°C-45°C) and thermophilic condition (45°C-65°C) [Nijaguna, 2002].

4.6.3.1 EFFECT OF TEMPERATURE ON DAILY BIOGAS PRODUCTION

Considering the result obtained from the above analysis the particle size of the biomasses, bamboo dust, saw dust and rice husk powder were made 0.355 mm by ball milling and sieving whereas sugarcane bagasse and rice straw were pretreated by ball milling to make fine strands. The biomasses are mixed with cattle dung in 1:3 ratio thus adjusting the C:N of the mixture. Water was added to the mixture in 1:3 ratio to make total solid of the feedstock 8-9%.

Daily variation of biogas production from cattle dung is shown in Fig. 4.6. It is observed that biogas production is the highest at 55°C followed by that of at 50°C. Third highest biogas production is obtained at 35°C. Biogas production at 40°C and 45°C is not found to be quite satisfactory. This is attributed to the fact that specific growth rate of bacteria depends upon the temperature and is the maximum between 30°C to 35°C in mesophilic condition [Sinclair and Kristiansen, 1993] and bacterial growth corresponds to biogas production [Budiyono et al., 2010]. Most of the biogas production is obtained within 30 days of HRT. The reason is that in batch mode anaerobic digestion process a fixed amount of volatile solid is used for biogas production which almost gets exhausted within 30 days of HRT thus reducing the biogas production after 30 days of HRT.

Similarly daily variation of biogas production from saw dust, sugarcane bagasse, rice straw, rice husk powder and bamboo dust mixed with cattle dung is shown in Fig. 4.7 to 4.11, respectively. The gas production from all the biomasses starts from second to third days of installing the digesters, except rice husk, where the gas production don't start upto fifth day. In case of saw dust and cattle dung mixture as shown in Fig. 4.7 the highest gas production (424 ml) is obtained at 55°C between 15-20th day. After that gas production starts declining. At 50°C also, highest gas production is obtained between 15-20th day. At 45°C and 35°C, highest production is achieved between 20-25th day, whereas at 40°C, it is found to be the highest between 15-20th day. In the first 15 days of HRT gas production is found to vary from 26 to 78 ml/day at 55°C. However in the next 15 days gas production varies from 53 to 84 ml/day at the same temperature. Although the gas production is continued till 50 days of HRT, gas production starts falling after 30 days of

HRT. The reason is same as that of cattle dung as explained earlier. Similar trend is observed at the other temperatures also, but the gas production rate is comparatively lower.

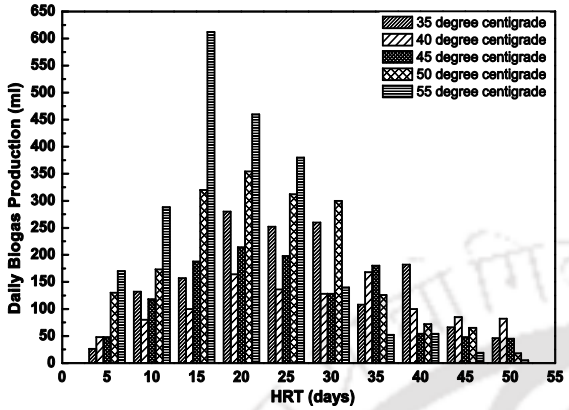


Fig. 4.6 Daily variation of biogas production by cattle dung

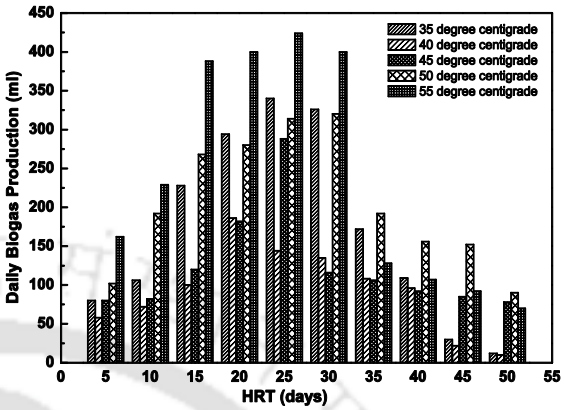


Fig. 4.7 Daily variation of biogas production by saw dust and cattle dung mixture

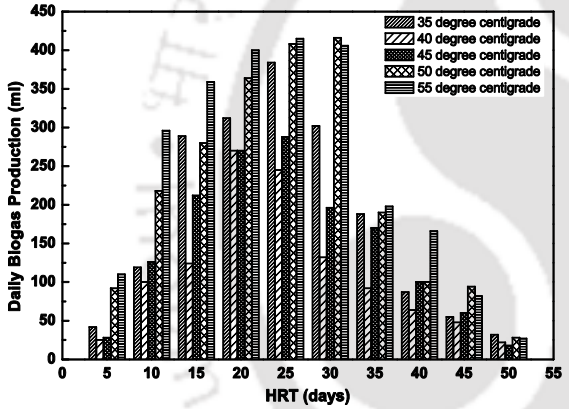


Fig. 4.8 Daily variation of biogas production by sugarcane bagasse and cattle dung mixture

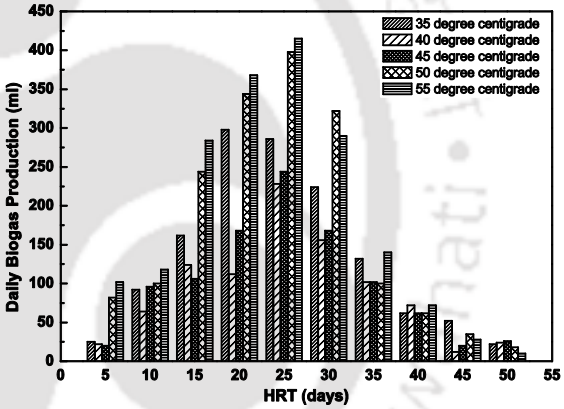


Fig. 4.9 Daily variation of biogas production by rice straw and cattle dung mixture

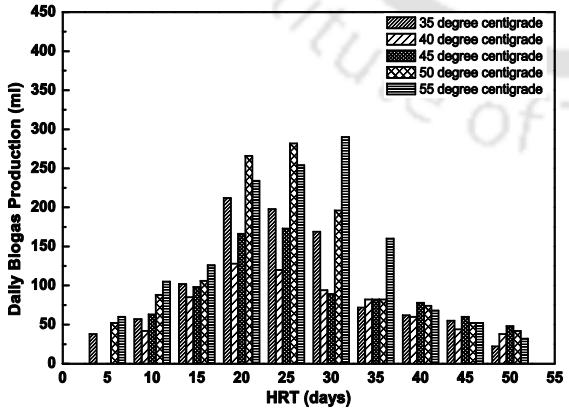


Fig. 4.10 Daily variation of biogas production by rice husk powder and cattle dung mixture

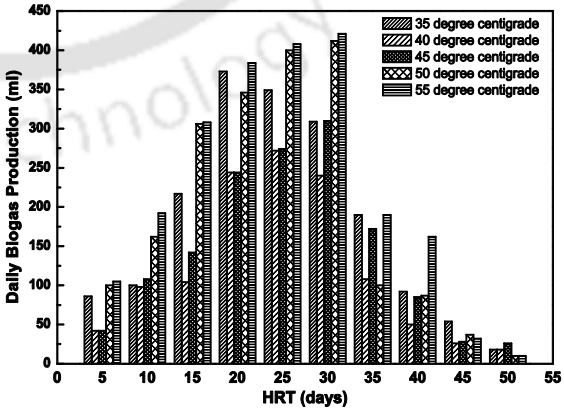


Fig. 4.11 Daily variation of biogas production by bamboo dust and cattle dung mixture

Similar is the case with sugarcane bagasse, rice husk powder and bamboo dust where the highest biogas production is achieved at 55°C between 25-30 days of HRT. On the other hand for saw dust and rice straw, highest biogas production is obtained between 20-25 days for at almost all the temperatures. Biogas production after 25-30 days of HRT was not found to be significant for the biomasses.

4.6.3.2 EFFECT OF TEMPERATURE ON CUMULATIVE BIOGAS PRODUCTION

Cumulative biogas production obtained from batch biomethanation of cattle dung at temperatures of 35°C to 55°C at a step of 5°C for a period of 50 days HRT is depicted in Fig. 4.12. It is observed that maximum biogas production is obtained at temperature 55°C followed by 50°C, 35°C, 45°C and 40°C, respectively. In mesophilic condition biogas production is found to be the highest at 35°C temperature whereas in thermophilic condition biogas production is the highest at 55°C temperature. It is observed that at 55°C and 50°C temperature biogas production is quite significant from the starting of the digestion period whereas at 35°C, 40°C and 45°C temperature biogas production become prominent after 10 days of HRT. On the other hand biogas production at 35°C and 45°C temperature is almost same till 25 days of HRT. After that biogas production at 45°C temperature starts declining significantly. Similar is the case with biogas production by the lignocellulosic biomass co-digested with cattle dung as shown in Fig. 4.13 to 4.17, where highest biogas production is obtained at 55°C followed by 50°C, 35°C, 45°C and 40°C temperature, respectively.The behaviour of the curves can be attributed to the fact that temperature is the most important ambient condition for bacterial growth [Ingraham, 1962] and it is reported in literature that biogas production is a function of bacterial growth in batch digesters [Budiyono et al., 2010]. Sinclair and Kristiansen, 1993 stated that specific growth rate of microorganisms is the highest at 35°C and gradually fall down with increase in temperature till 45°C.

Figure 4.13 shows the cumulative biogas production by saw dust mixed with cattle dung at different temperature. It is observed that at 55°C temperature biogas production is significantly higher than that of other temperatures from the starting of digestion. Biogas production at 50°C and 35°C temperature was almost equivalent till 35 days of HRT. After that biogas production at 35°C temperature declines considerably. Biogas production at 40°C and 45°C temperature is found to be very insignificant. Cumulative biogas production by sugarcane bagasse and bamboo

dust mixed with cattle dung is found to be quite satisfactory as shown in Fig. 4.14 and 4.17 respectively. But cumulative biogas production by rice straw and rice husk powder mixed with cattle dung is not found to be promising as shown in Fig. 4.15 and 4.16 respectively. Total biogas production by rice straw mixed with cattle dung is found to be higher than that of rice husk powder mixed with cattle dung at all the temperature condition. This can be attributed to the fact that rice straw also acts as a good support media for microorganisms which help it in bacterial growth [Andersson and Björnsson, 2002].

It is observed that in thermophilic condition (55°C) the highest biogas production is obtained from sugarcane bagasse mixed with cattle dung (38.26 ml/g VS), followed by saw dust (37.57 ml/g VS), bamboo dust (33.89 ml/g VS), rice straw (32.93 ml/g VS) and rice husk (22.74 ml/g VS) mixed with cattle dung. Whereas in typical mesophilic condition (35°C) highest biogas production is achieved from sugarcane bagasse mixed with cattle dung (28.16 ml/g VS), followed by bamboo dust (27.39 ml/g VS), saw dust (26.57 ml/g VS), rice straw (24.42 ml/g VS) and rice husk (15.45 ml/g VS) mixed with cattle dung. The reason for variation of biogas production from different biomasses mixed with cattle dung is that digestibility of biomass depends upon the lignin to cellulose ratio which is different for different biomasses. On the other hand reason for variation of biogas production in mesophilic and thermophilic condition for the same biomass is that with increase in temperature digestibility of biomass increases due to decrease in lignin to cellulose ratio which eventually leads to the higher biogas production.

The measurement of methane and carbon di-oxide contents in biogas obtained from various biomasses is carried out in gas chromatograph (GC) analyser [model No. CHEMITO CERES 800 plus]. It is found that methane content of biogas produced from the biomass considered in the present study varies between 60 to 67%, whereas for cattle dung it was found to be 58%. Gas chromatography results of biogas produced from the biomass considered in the present study are shown in Appendix V.

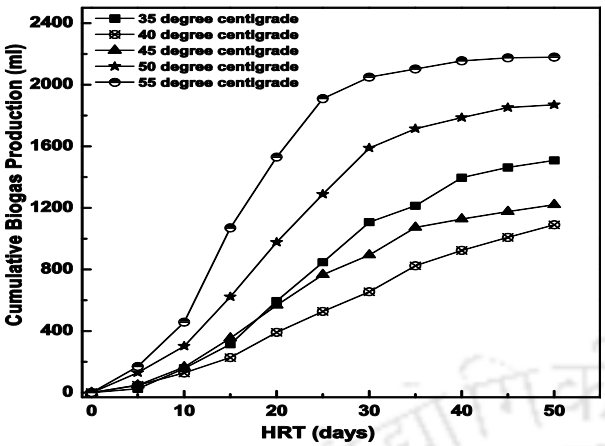


Fig. 4.12 Cumulative biogas production by pure cattle dung (ml)

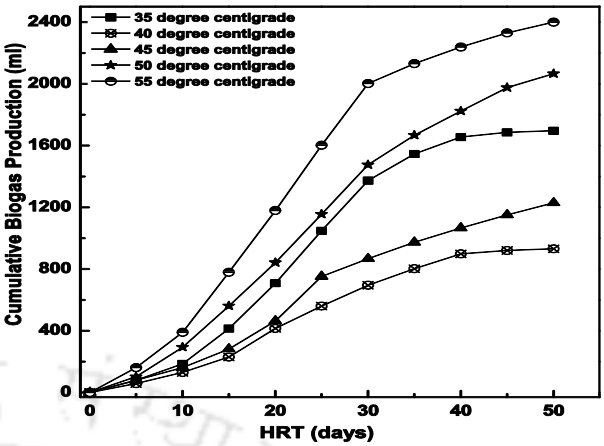


Fig. 4.13 Cumulative biogas production by saw dust mixed with cattle dung (ml)

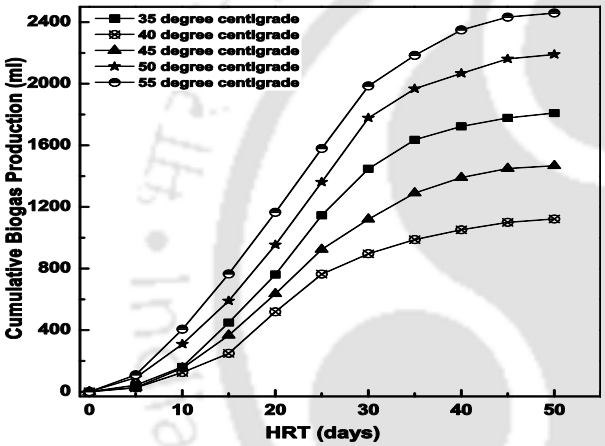


Fig. 4.14 Cumulative biogas production by sugarcane bagasse mixed with cattle dung(ml)

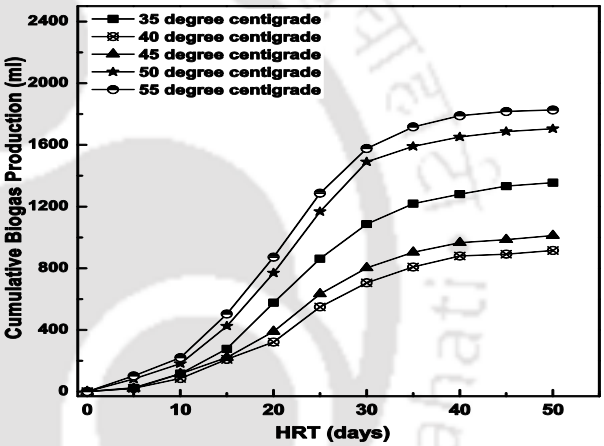


Fig. 4.15 Cumulative biogas production by rice straw mixed with cattle dung (ml)

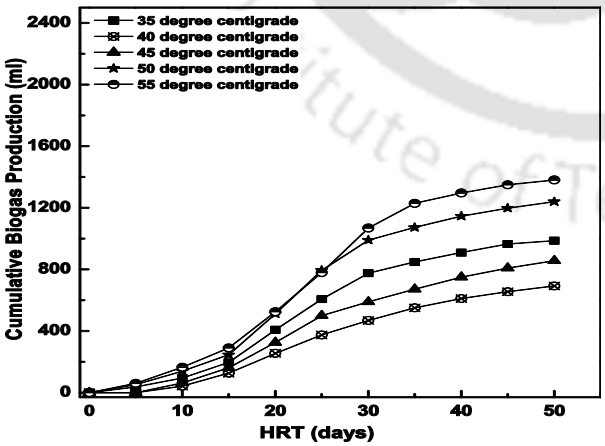


Fig. 4.16 Cumulative biogas production by rice husk powder mixed with cattle dung (ml)

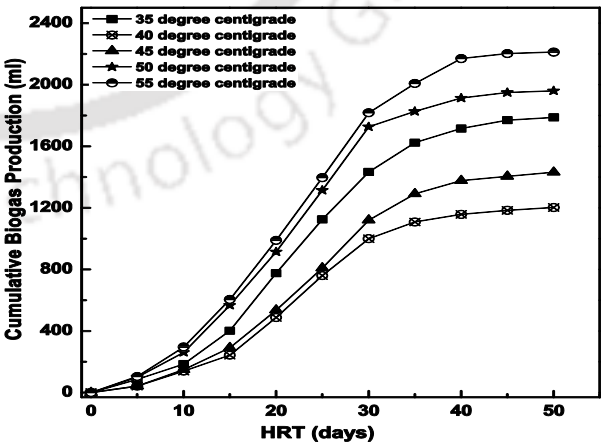


Fig. 4.17 Cumulative biogas production by bamboo dust mixed with cattle dung (ml)

4.6.4 EFFECT OF CO-DIGESTION OF BIOMASS WITH CATTLE DUNG

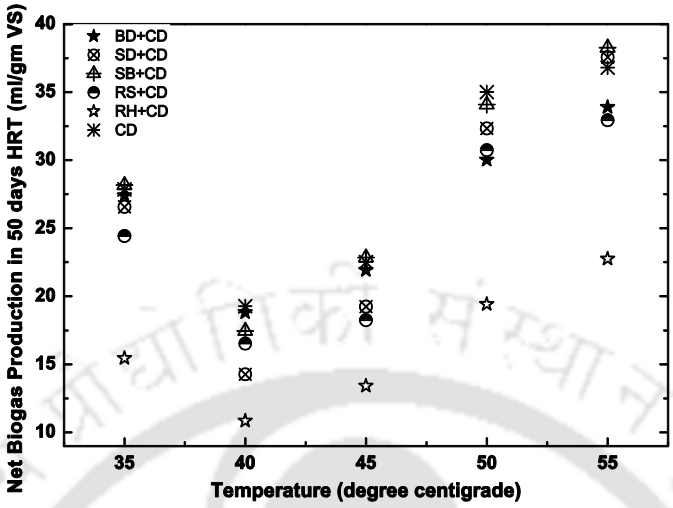


Fig. 4.18 Effect of co-digestion and temperature on net biogas production

Figure 4.18 shows the results of net biogas production from the co-digestion of cattle dung with lignocellulosic biomass such as bamboo dust, saw dust, sugarcane bagasse, rice straw and rice husk powder at different temperatures. It is observed that with increase in temperature of the substrate from 35°C to 40°C, total biogas production decreases. Whereas with increase in temperature from 40°C to 55°C the net biogas production increases for all the feed stocks. This is due to the higher specific growth rate of microorganisms at 35°C than that of at 40°C [Sinclair and Kristiansen, 1993]. It is observed from the figure that net biogas production per g VS for saw dust, bamboo dust, sugarcane bagasse and rice straw co-digested with cattle dung is found to be within ±5 ml/g VS of net biogas production per g VS from pure cattle dung. Whereas for rice husk co-digested with cattle dung the net biogas production per g VS is observed to be within ±16 ml/g VS of net biogas production per g VS from pure cattle dung. Here the biogas production from bamboo dust, saw dust, sugarcane bagasse mixed with cattle dung can be attributed to their almost equivalent lignin to cellulose ratio which indicates the digestibility of biomass [Sharma et.al, 1988], whereas earnest biogas production from rice straw may be attributed to its role as biofilm carrier which help it in better biogas production [Andersson and Björnsson, 2002].

It is also seen that in thermophilic condition biogas production from sugarcane bagasse and saw dust mixed with cattle dung are found to be higher than that of pure cattle dung under the same

condition. Whereas in mesophilic condition biogas production from only sugarcane bagasse mixed with cattle dung is found to be higher than that of cattle dung under the same condition. Rest of the biomass mixed with cattle dung produces biogas lesser than that of pure cattle dung.

4.6.5 EFFECT OF ADDITION OF BIOCHAR ON BIOGAS PRODUCTION

Bio-char is nothing but charcoal which is obtained from the carbonization of biomass.It shows a rough, highly porous surface area, with both micro and macro structures that will allow organisms to adhere to their surface. Indeed the size of the pore structure will determine whether biofilms develop only on the surface or also within the internal structure of the char. These characteristics make biochar a potential candidate as a cheap and available resource for microbial cell immobilization in anaerobic digesters. This study will look at the effectiveness of increasing digestion and stability by investigating the use of biochar as a biofilm carrier.It is observed from the Fig. 4.19 that with addition of bio-char the production of biogas from cattle dung can be improved. Results show that the biogas production increases with the increase of biochar addition from 0 to 5% of TS of the substrate. It is also observed that with addition of biochar amounting 10% of TS to the cow dung, the biogas production become very insignificant. From the result it can be concluded that too much biochar on cattle dung has detrimental effect on biogas production.

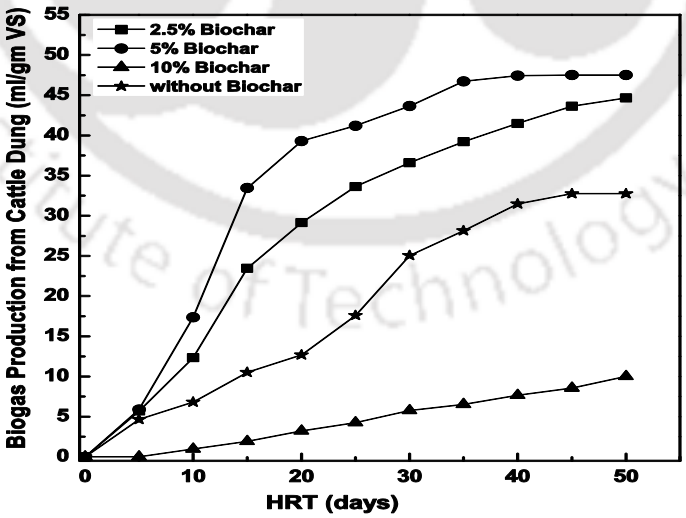


Fig. 4.19 Effect of biochar on biogas production from cattle dung

4.7 SUMMARY

From the parametric study of biogas production from lignocellulosic biomass mixed with cattle dung, it can be concluded that different parameters affect the biogas generation from substrates in different way. It is observed that with decrease in particle size of feedstock, biogas generation increases. On the other hand biogas production from lignocellulosic biomass mixed with cattle dung is found to be optimum at 8-9% TS. It is also observed that with increase in temperature biogas production increases within the range 40-55°C and with addition of additives like biochar in appropriate proportion, biogas production can be improved. Chapter 5 discusses the kinetic study on biogas production from selected lignocellulosic biomasses mixed with cattle dung using first order kinetic equation as well as modified Gompertz equation. Based on the results of kinetic study the modified Gompertz equation is reformed for mesophilic as well as thermophilic range of temperature.

CHAPTER 5

KINETIC STUDY OF BIOMETHANATION PROCESSES

5.1 INTRODUCTION

The study of kinetics of biodegradation process is very important to know about the performance of reactor and helps in the design of the biogas plant operating with various feed materials. It also helps in understanding the mechanisms behind anaerobic digestion process [Castilo et al., 1995, Abdullahi, 2011, Mata-Alvarez et al., 1993]. Kinetic models are reported to be useful tool to optimize the co-digestion processes as well [Gavala et al., 2003]. Several kinetic models pertaining to biomethanation process have been reported during the last few decades. Although temperature is the most important ambient condition for bacterial growth [Ingraham, 1962], temperature dependency of biogas digestion is not that revealing in most of the models. However, appropriate mathematical models are needed in order to overcome the problem of instability of system and also to design and operate anaerobic systems effectively as discussed in chapter 2 of this thesis.

This chapter presents the kinetic study of biogas production from lignocellulosic biomass mixed with cattle dung. As discussed in previous chapter cattle dung is mixed with the biomass in 1:3 ratio to optimize the C:N in permissible limit for production of biogas effectively and also to introduce methanogenic bacteria into the substrate. It also presents the effect of temperature on the kinetics of biogas production from the substrate. The investigation is performed at five different temperatures 35°C to 55°C at a step of 5°C, respectively in 1000 ml volume digesters in batch mode. The working volumes of the biodigesters are maintained at 900 ml volume and ran under controlled temperature. The various substrates considered are saw dust, rice straw, rice husk powder, sugarcane bagasse and bamboo dust each mixed with cattle dung. Water is added to these mixtures in 1:3 ratio so as to control the TS around 8-9% in the substrate. The cumulative biogas production is observed for 50 days of HRT. It presents the kinetic parameters from mathematical model concerning biogas production rate in batch anaerobic digestion processes assuming that the biogas production rate in batch mode corresponds to the specific growth rate of methanogenic bacteria in the biodigesters.

5.2 APPLICATION OF FIRST ORDER KINETIC MODEL TO BIOGAS GENERATION

The kinetics of digestion process is crucial in determining the rate of gas production per unit mass of volatile solid. Using chemical engineering theory, a description of batch digestion kinetics is obtained [Wise, 1981; Mittal, 1996]. For first order kinetics, the rate of degradation of the volatile solids is given by

$$\frac{dC_B}{dt} = -kC_B \tag{5.1}$$

where

C_B = the substrate concentration or concentration of biodegradable volatile solids (VS)

k = the first order kinetic rate constant

t = the time

Rearranging Eq. (5.1)

$$\frac{dC_B}{C_B} = -kdt \tag{5.2}$$

Integrating both sides we get,

$$\int_{C_0}^{C_t} \frac{dC_B}{C_B} = -\int_0^t kdt \tag{5.3}$$

or,

$$\ln\left(\frac{C_t}{C_0}\right) = -kt \tag{5.4}$$

or,

$$\frac{C_t}{C_0} = \exp(-kt) \tag{5.5}$$

Linke, 2006, correlated the transformation of biodegradable solids (C) into biogas (y) at time t as shown in Fig. 5.1 [Yusuf et al., 2011]. The biodegradable fraction of the complex organic substrate is converted to biogas according to Eq. (5.6).

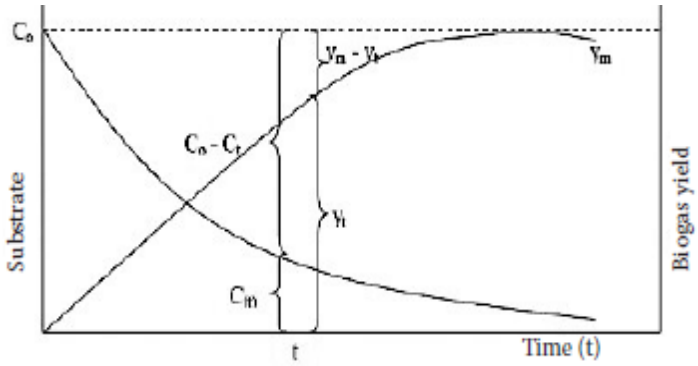


Fig. 5.1 Correlation between substrate degradation and biogas production in course of time [Linke, 2006]

$$\frac{y_m}{y_m - y_t} = \frac{C_0}{C_t} \tag{5.6}$$

or,

$$\frac{y_m - y_t}{y_m} = \frac{C_t}{C_0} \tag{5.7}$$

Now, replacing $\frac{C_t}{C_0}$ in Eq. (5) with $\frac{y_m - y_t}{y_m}$, we have

$$\frac{y_m - y_t}{y_m} = \exp(-kt) \tag{5.8}$$

or,

$$y_t = y_m \{1 - \exp(-kt)\} \tag{5.9}$$

where

y_t= volume of biogas produced per unit mass of volatile solids fed at any time, t (ml/g)

y_m=volume of biogas produced per unit mass of volatile solids converted at maximum time (ml/g)

k= kinetic rate constant (day^{-1})

t= time of digestion (days)

Evaluation of substrate biodegradability and kinetic rate constant was done by linearizing Eq. (5.9) [Yusuf et al., 2011].

Differentiating Eq. (5.9),

$$\frac{dy_t}{dt} = y_m k \exp(-kt) \tag{5.10}$$

Taking natural logarithm on both sides of the equation,

$$\ln\left(\frac{dy_t}{dt}\right) = \left(\ln y_m + \ln k\right) - kt \tag{5.11}$$

This equation was further reduced to the following form,

$$\frac{1}{t}\ln\left(\frac{dy_t}{dt}\right) = \frac{1}{t}\left(\ln y_m + \ln k\right) - k \tag{5.12}$$

Equation (5.12) which is the modified first order equation is analogous to straight line equation, i.e, $y=mx+c$.

where

$\left(\ln y_m + \ln k\right)$ = the slope

-k= the intercept of the graph of $\frac{1}{t}\ln\left(\frac{dy_t}{dt}\right)$ vs inverse of the hydraulic retention time (1/t)

Thus the first order kinetic rate constant, k can be easily determined from the plot of $\frac{1}{t}\ln\left(\frac{dy_t}{dt}\right)$ vs inverse of the hydraulic retention time (1/t).

The term (-k) is a measure of the rate of removal of the biodegradable fractions as the biogas production increases with time. According to Eastman and Ferguson, 1981, the first order kinetic constant k is a pure empirical function which represents the cumulative effects of many parameters such as pH, temperature, quantity and quality of substrate, rate of removal of biodegradable fractions, rate of inhibition by other components of the substrate e.g. lignin or by-product of the reaction process such as fatty acids etc. The more negative the value of k, the faster the rates of removal of the biodegradable fractions while more the positive value of k, the slower the rate of removal of the biodegradable fractions [Yusuf et al., 2011]. Thus Eq. (5.12) can be used to detect anaerobic digestion whether it is progressive or regressive. The modified first order equation is used to simulate the experimental data of biogas generation from bamboo

dust (BD), saw dust (SD), sugarcane bagasse (SB), rice straw (RS) and rice husk (RH) mixed with cattle dung along with pure cattle dung at temperatures 35°C to 55°C at an interval of 5°C.

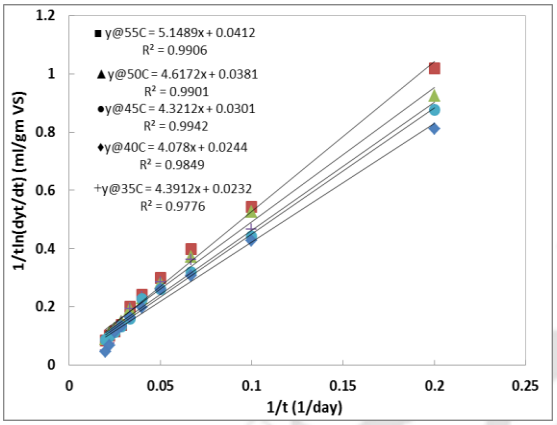


Fig. 5.2 Plot of $\frac{1}{t}\ln\left(\frac{dy_t}{dt}\right)$ against 1/t for SD

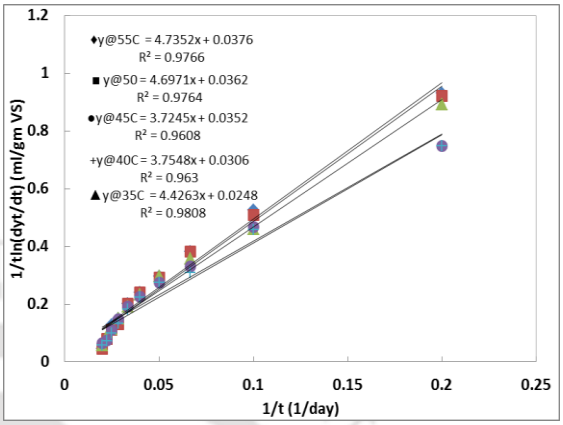


Fig. 5.3 Plot of $\frac{1}{t}\ln\left(\frac{dy_t}{dt}\right)$ against 1/t for BD

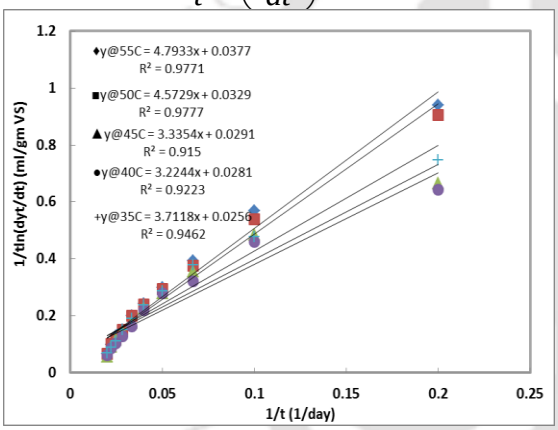


Fig. 5.4 Plot of $\frac{1}{t}\ln\left(\frac{dy_t}{dt}\right)$ against 1/t for SB

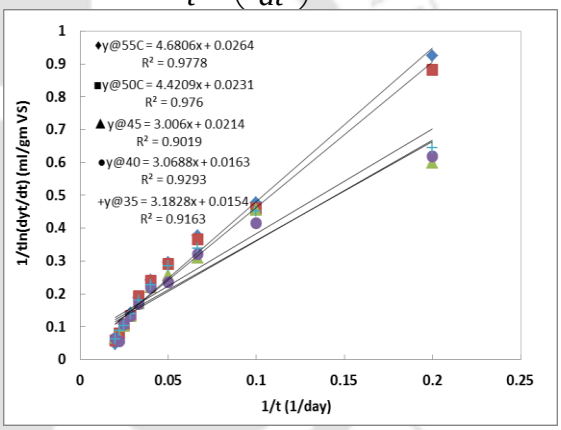


Fig. 5.5 Plot of $\frac{1}{t}\ln\left(\frac{dy_t}{dt}\right)$ against 1/t for RS

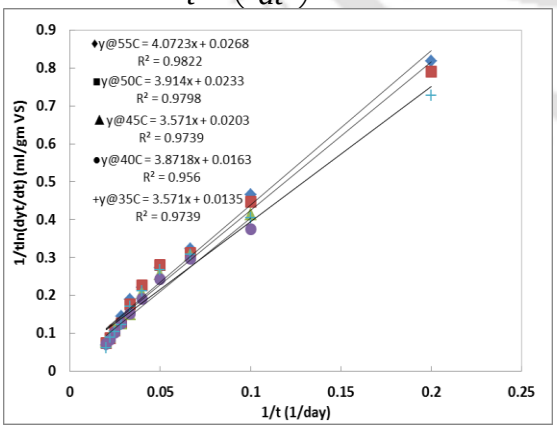


Fig. 5.6 Plot of $\frac{1}{t}\ln\left(\frac{dy_t}{dt}\right)$ against 1/t for RH

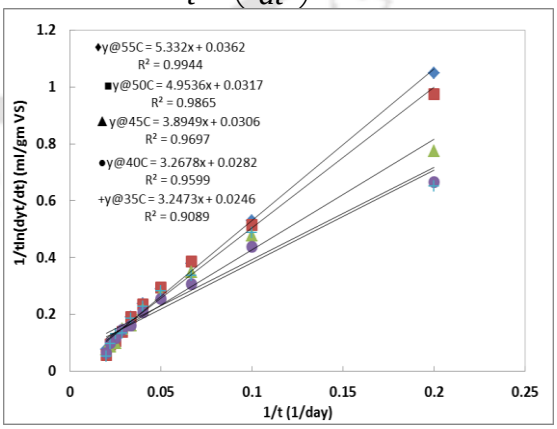


Fig. 5.7 Plot of $\frac{1}{t}\ln\left(\frac{dy_t}{dt}\right)$ against 1/t for CD

Fig. 5.2 represents the graph of $\frac{1}{t}\ln\left(\frac{dy_t}{dt}\right)$ vs 1/t for saw dust mixed with cattle dung in 1:3 ratio. It is observed from the graph that the linear trendline fits well with that of the experimental value with regression co-efficient, R^2=0.977, 0.984, 0.994, 0.990 and 0.990 for temperatures 35°C, 40°C, 45°C, 50°C and 55°C respectively. Similarly, Fig. 5.3 to 5.7 represents the graph of $\frac{1}{t}\ln\left(\frac{dy_t}{dt}\right)$ vs 1/t for bamboo dust, sugarcane bagasse, rice straw, rice husk powder each mixed with cattle dung in 1:3 ratio and pure cattle dung respectively. It is seen that in all the cases the linear trendline fits quite well with the experimental data with regression co-efficient, R^2>0.90.

5.2.1 EFFECT OF TEMPERATURE ON KINETIC RATE CONSTANTS

Table 5.1 presents the kinetic rate constant of cattle dung at temperatures 35°C to 55°C at a step of 5°C. It is observed that with increase in temperature kinetic rate constant, k of cattle dung turn out to be more negative and become the maximum at temperature 55°C indicating faster biodegradation process [Yusuf et.al, 2011]. Kinetic rate constant k obtained from the present result for cattle dung as feed material at 35°C is -0.024. Under the same condition, Abdullahi et al., 2011 found kinetic rate constant, k to be -0.31 for cattle dung. A deviation of 22.5% for the value of kinetic rate constant, k in present study is observed as compared to literature.

Table 5.1 Kinetic rate constant of cattle dung at different temperature

Temperature (°C)	**Kinetic rate constant, k (s^{-1})**	**Kinetic rate constant, k (s^{-1})**	**% Variation of present result with literature**
	Present Study	Literature	
35	-0.024	-0.031 [Abdullahi et al., 2011]	22.5
40	-0.028	……..	……..
45	-0.030	……..	……..
50	-0.031	……..	……..
55	-0.036	……..	……..

Table 5.2 shows the kinetic rate constant of bamboo dust, saw dust, sugarcane bagasse, rice straw and rice husk mixed with cattle dung in 1:3 ratio at temperature 35°C to 55°C at an interval of 5°C. Like cattle dung the kinetic rate constant, k is increasing with increase in temperature from 35 to 55°C. Also, with increase in temperature of the digestate the kinetic rate contestant, k become more negative which indicates that the biodegradation process of organic matter in biomass become faster with increase in temperature [Yusuf et al., 2011].

Table 5.2 Kinetic rate constants of lignocellulosic biomasses at different temperature

Temperature (°C)	**Kinetic rate constant, k (s^{-1})**				
	Saw Dust + Cattle Dung	**Bamboo Dust + Cattle Dung**	**Sugarcane Bagasse + Cattle Dung**	**Rice Straw + Cattle Dung**	**Rice Husk + Cattle Dung**
35	-0.023	-0.024	-0.025	-0.015	-0.013
40	-0.024	-0.030	-0.028	-0.016	-0.016
45	-0.030	-0.035	-0.029	-0.021	-0.020
50	-0.038	-0.036	-0.032	-0.023	-0.023
55	-0.041	-0.037	-0.037	-0.026	-0.026

5.3 MODIFIED GOMPERTZ MODEL APPLIED TO EXPERIMENTAL DATA

First order kinetic model is extensively used by many researchers for kinetic study due to the simplicity and ease in evaluation. This model, however, does not reveal the production potential, maximum production rate and lag phase period of biogas generation. Moreover, the degradation of complex substrates is difficult to describe with kinetic model with single parameter [Contois (1959)]. Thus an alternate form of model is needed to know the biomethanation process in details. Modified Gompertz model as described in Chapter 2 gives higher coefficient of regression (R^2) as compared to other kinetic models [Lo et al., 2010]. Many researchers have applied the same model successfully to study bacterial growth [Zwietering et al., 1990 and Lay et al., 1996], biomethanation of vinass**e** waste [Budiyono et al., 2013] and cattle dung [Budiyono et al., 2010]. Present section deals with use of this model for biomethanation process with

lignocellulosic biomass as feed material. Subsequently, effect of temperature is introduced in the modified Gompertz model based on the experimental data of the present study.

The modified Gompertz equation which gives the cumulative biogas production from batch digesters assumes that biogas production rate corresponds to specific growth rate of methanogenic bacteria in the digester [Budiyono et al., 2010; Nopharatana et al., 2007 and Yusuf et al., 2011]. Equation 5.13 presents the modified Gompertz equation as given below

$$P = A.\exp\{-\exp[\frac{Ue}{A}(\lambda - t) + 1]\} \tag{5.13}$$

where

P is the cumulative of the specific biogas production (ml/g VS)

A is the biogas production potential (ml/g VS)

U is the maximum biogas production rate (ml/g VS/day)

λ is the lag phase period or the minimum time required to produce biogas (day)

e is the mathematical constant having value 2.718282

t is the time period of biogas production (day)

5.3.1 EFFECT OF TEMPERATURE ON KINETIC CONSTANTS

The present study is carried out at five different temperatures viz. 35°C to 55°C at a step of 5°C to evaluate the effect of temperature on kinetic parameters of modified Gompertz model. The cumulative biogas production from lignocellulosic biomass mixed with cattle dung is simulated using modified Gompertz model and the experimental data of biogas accumulation are plotted along with the model data in cumulative biogas production vs HRT plot. Figure 5.8 represents the experimental data along with the model data of cumulative biogas production of saw dust mixed with cattle dung vs HRT at five different temperatures. It shows that the model data fits quite well with that of the respective experimental data with co-efficient of regression (R^2) 0.99 for all the temperatures. Similar is the case with rice straw, rice husk powder, sugarcane bagasse and bamboo dust mixed with cattle dung as shown in Fig. 5.9-5.12. Figure 5.13 shows the comparison of experimental and model data for cattle dung and it is observed that model data fits well with the experimental data with co-efficient of regression (R^2) 0.99.

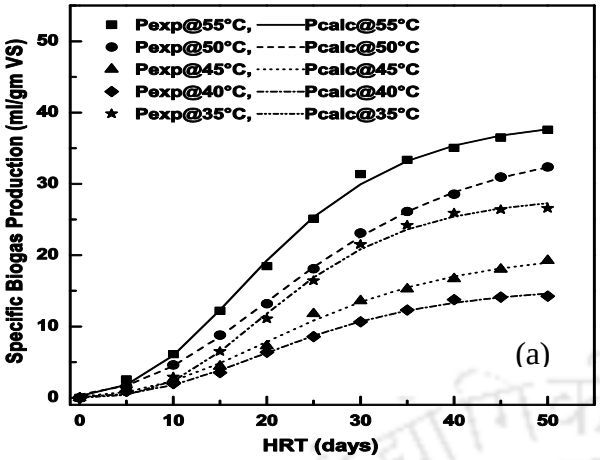


Fig. 5.8 Comparison of experimental and model data for saw dust

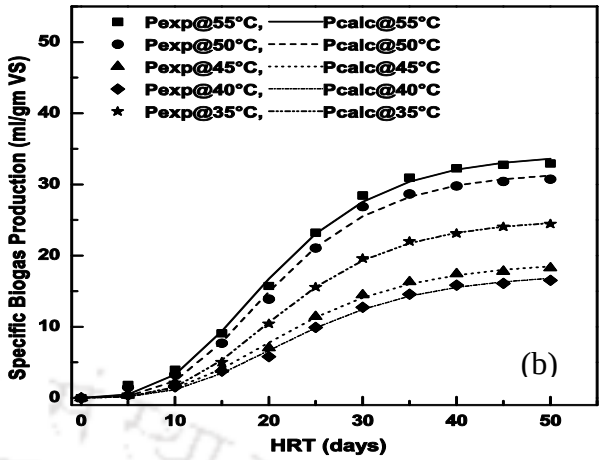


Fig. 5.9 Comparison of experimental and model data for rice straw

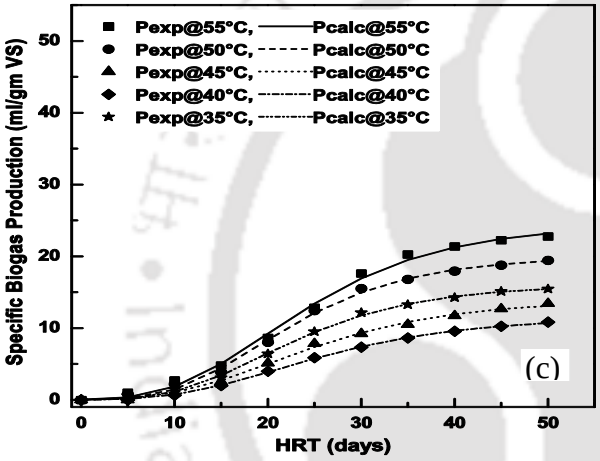


Fig. 5.10 Comparison of experimental and model data for rice husk powder

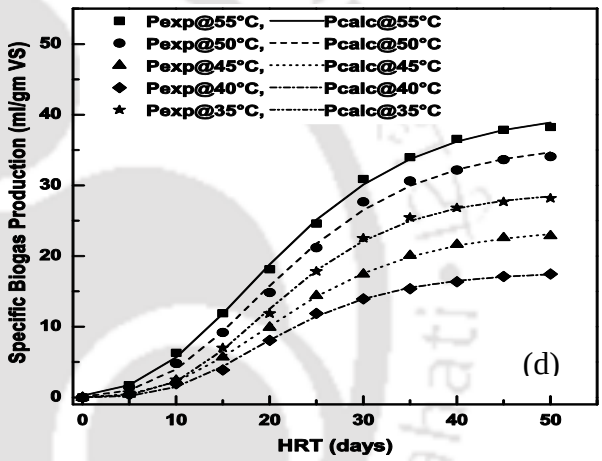


Fig. 5.11 Comparison of experimental and model data for sugarcane bagasse

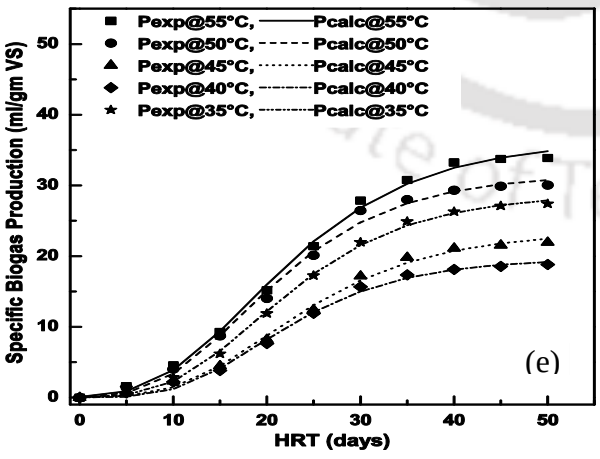


Fig. 5.12 Comparison of experimental and model data for bamboo dust

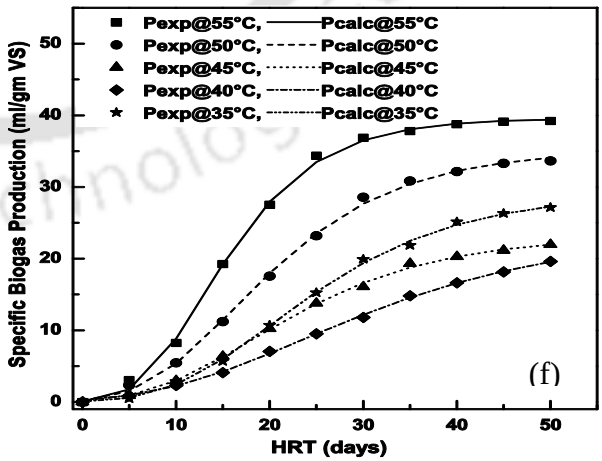


Fig. 5.13 Comparison of experimental and model data for cattle dung

The experimental data is analyzed using non-linear regression for determining the kinetic constants A, U and λ of the modified Gompertz model. Table 5.2 depicts the comparison of kinetic constants at different temperatures for saw dust, rice straw, rice husk powder, sugarcane bagasse and bamboo dust mixed with cattle dung in 1:3 ratio along with that of pure cattle dung. It is observed from the table that at 55°C, all the substrates exhibit highest biogas production rate followed by 50°C, 35°C, 45°C and finally 40°C temperature. In thermophilic condition highest biogas production potential, maximum biogas production rate and lowest lag phase period is obtained at 55°C. In mesophilic condition highest biogas production potential and maximum biogas production rate is obtained at 35°C. In case of saw dust, rice straw, and sugarcane bagasse mixed with fresh cattle dung, lag phase period or minimum time required to produce biogas in mesophilic condition is lowest at 35°C. In case of bamboo dust mixed with fresh cattle dung, lag phase period is lowest at 40°C respectively.

The biogas production potential of the biomass at 55°C is the highest in case of sugarcane bagasse mixed with cattle dung (40.744 ml/g VS) followed by saw dust (39.106 ml.g VS), bamboo dust (36.278 ml/g VS) and rice straw (34.317 ml/g VS) mixed with cattle dung.

The maximum biogas production rate of the biomasses is found to be highest in case of saw dust (1.406 ml/g VS/day) followed by sugarcane bagasse (1.405 ml/g VS/day), rice straw (1.493 ml/g VS/day) and bamboo dust (1.340 ml/g VS/day) mixed with cattle dung.

At 35°C the biogas production potential (ml/g VS) of the biomass is found to be maximum for sugarcane bagasse (29.379/g VS) followed by bamboo dust (28.820 ml/g VS), saw dust (28.333 ml/g VS) and rice straw powder (25.201 ml/g VS) mixed with cattle dung.

Similarly, the maximum biogas production rate of the biomasses at 35°C temperature is observed to be highest in case of sugarcane bagasse (1.192 ml/g VS) followed by bamboo dust (1.151 ml/g VS), saw dust (1.091 ml/g VS) and rice straw (1.091 ml/g VS) mixed with cattle dung.

It is observed from the Table 5.3 that the behaviour of kinetic parameters at different temperatures follow almost similar trend for all the biomasses. In all the cases, the biogas production potential as well as the maximum biogas production rate is the highest at 55°C followed by 50°C, 35°C, 45°C and 40°C respectively.

The lag phase period of biogas production for all the temperature is found to be decreased exponentially with increase in temperature. This is due to the increased digestibility of biomass with increase in temperature.

Modified Gompertz plot had shown very good correlation (R^2=0.99) for simulating the cumulative biogas production. Table 5.3 shows the kinetic parameters of the modified Gompertz model at different temperature based on the experimental data from the present study.

Table 5.3 Kinetic parameters at different temperatures

Substrates/Temperatures		**35°C**	**40°C**	**45°C**	**50°C**	**55°C**
SD	A, (ml/g VS)	28.333	15.619	20.644	35.770	39.106
	U, (ml/g VS)	1.091	0.501	0.613	0.994	1.406
	λ, days	9.160	7.391	7.192	6.444	6.228
RS	A, (ml/g VS)	25.201	17.544	19.150	31.820	34.317
	U, (ml/g VS)	1.091	0.669	0.759	1.445	1.493
	λ, days	10.261	10.016	9.760	9.621	8.735
RH	A, (ml/g VS)	16.021	11.475	13.945	19.956	24.444
	U, (ml/g VS)	0.633	0.388	0.482	0.811	0.875
	λ, days	9.722	10.066	9.589	9.640	9.444
SB	A, (ml/g VS)	29.379	17.834	24.080	36.259	40.744
	U, (ml/g VS)	1.192	0.759	0.897	1.304	1.405
	λ, days	9.465	9.265	8.732	7.876	6.570
BD	A, (ml/g VS)	28.820	19.682	23.447	31.576	36.278
	U, (ml/g VS)	1.151	0.845	0.899	1.293	1.340
	λ, days	9.393	10.267	10.247	8.260	8.053
CD	A, (ml/g VS)	28.990	18.463	21.643	33.951	36.708
	U, (ml/g VS)	0.939	0.528	0.760	1.344	1.340
	λ, days	8.017	6.654	6.232	6.045	5.129

5.4 KINETIC MODEL DEVELOPMENT FOR BIOGAS PRODUCTION

Temperature plays a very important role in bacterial growth [Ingraham, 1962]. Normally reaction rate of a chemical reaction increases with increase in temperature, but temperature dependency of biogas digestion is not that revealing in most of the models. Modified Gompertz model fits quite well with the cumulative biogas generation from lignocellulosic biomass as shown in Fig. 5.8-5.13 but it does not show the effect of temperature on biogas production.

This study focuses on the development of a kinetic model which can showcase the effect of temperature on biogas production from lignocellulosic biomass co-digested with cattle dung. Therefore biogas production rates at temperatures 35°C -55°C at a step of 5°C was studied and the cumulative biogas production is simulated using modified Gompertz plots. While studying the kinetic parameters of the biomasses at different temperatures, it is observed that for all the above mentioned biomasses, the kinetic parameters follow similar trend of behaviour with change in temperature. Based on these, relationship between the kinetic parameters of the modified Gompertz model and temperature are developed and used them in the parent equation of the model. The suggested mathematical model gave satisfying conformity with the experimental data. The reformed form of the modified Gompertz equation is further validated with literature data and found that within the range 35°C to 55°C the reformed model presented quite satisfying results with the experimental data.

Figure 5.14 shows the effect of temperature on biogas production potential, A of above mentioned biomass. It is observed that the kinetic parameter, A for all the biomass changes with temperature in the same manner. When temperature was increasing from 35°C to 40°C, the biogas production potential decreased. But with increase in temperature from 40°C to 55°C the biogas production potential increased for all the biomasses. Similarly Fig. 5.15 shows the effect of temperature on maximum biogas production rate, U of various lignocellulosic biomasses and it is observed that maximum biogas production rate first decreases with increase in temperature from 35 to 40°C and then increases with increase in temperature from 40 to 55°C. The high amount of biogas production potential, A and maximum biogas production rate, U at 35°C in mesophilic condition and at 55°C in thermophilic condition is probably due to large microbial activity in mesophilic and thermophilic temperature range respectively [Mahanta et al., 2004]. The biogas production potential, A and maximum biogas production rate, U are functions of

biogas generation which corresponds to specific growth rate of methanogenic bacteria [Budiyono et al., 2010]. On the other hand, variation of lag phase period with temperature is shown in Fig. 5.16. It is observed from the figure that with increase in temperature from 35 to 55°C the minimum time required for biogas production decreases. This is due to the fact that thermal pre-treatment is one of the important factors to improve the anaerobic digestion of lignocellulosic biomasses which enhance the hydrolysis process by breaking the lignin faster [Usman et al., 2012].

The kinetic parameters of all the above mentioned lignocellulosic biomass are almost equivalent to each other except rice husk powder. For rice husk powder the biogas production potential, A and maximum biogas production rate, U are quite low as compared to the other lignocellulosic biomass considered for the experiment. That is why the kinetic parameters of rice husk powder were not considered for developing the kinetic model for lignocellulosic biomass. Since the kinetic parameter, A of saw dust, bamboo dust, sugarcane bagasse and rice straw mixed with cattle dung are quite close to each other at each distinguished temperature, that is why average of the parameter is taken at each considered temperature. The effect of temperature on mean value of biogas production potential, A of above mentioned biomass is shown in Fig. 5.17. For the sake of simplicity the range of temperature is taken from 40 to 55°C. In the similar manner mean of maximum biogas production rate as well as lag phase period is calculated and plotted in Fig. 5.18 and 5.19, respectively. Non-linear curve fitting is done to the graphs of Fig. 5.17 to 5.19 and found that the trendline fit into an exponential form of equation as shown in Eq. 5.14 with regression co-efficient R^2=.0.951, 0.935 and 0.955, respectively.

$$y = y_0 . e^{R_0 x} \tag{5.14}$$

After doing the curve fitting of the parameters, A, U and λ with the experimental data the following three equations are obtained as shown by Eq.15-17.

$$A = 2.0264 \times e^{0.0541 \times t} \tag{5.15}$$

$$U = 0.0845 \times e^{0.0519 \times t} \tag{5.16}$$

$$\lambda = 17.512 \times e^{-0.016 \times t} \tag{5.17}$$

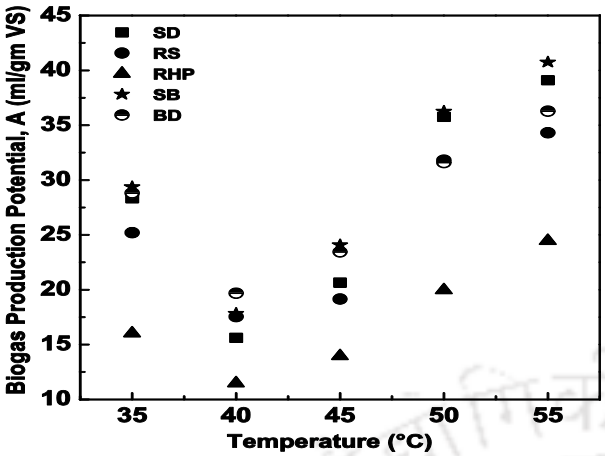


Fig. 5.14 Effect of temperature on Biogas production potential, A

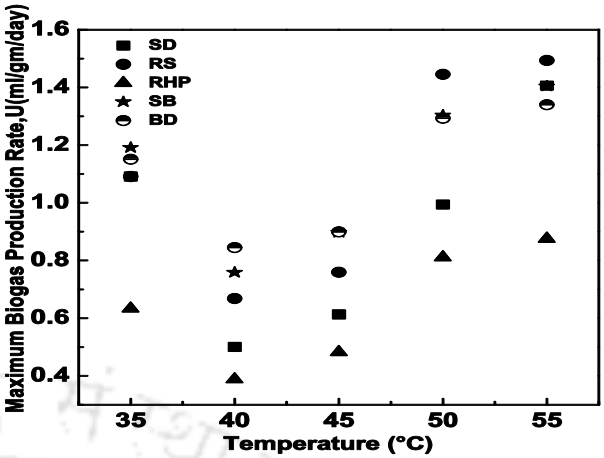


Fig. 5.15 Effect of temperature on Maximum Biogas production rate, U

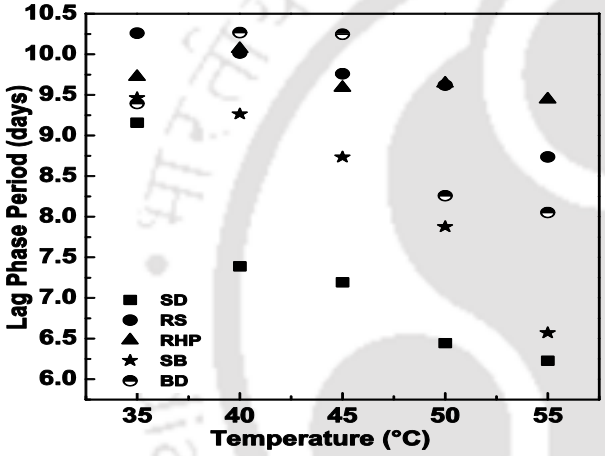


Fig. 5.16 Effect of temperature on lag phase period, λ

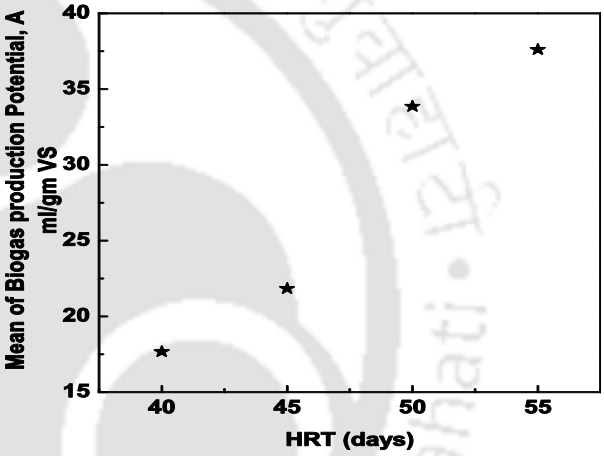


Fig. 5.17 Effect of temperature on mean value of biogas production potential, A

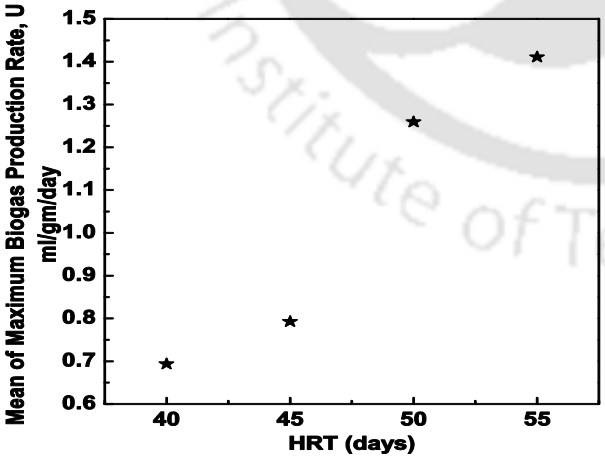


Fig. 5.18 Effect of temperature on mean value of Maximum Biogas production rate, U

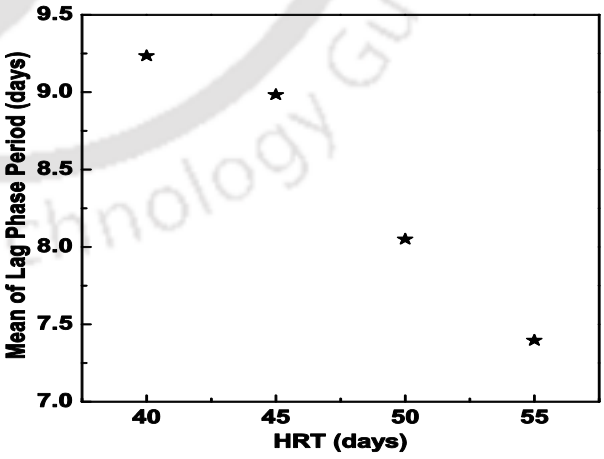


Fig. 5.19 Effect of temperature on mean value of lag phase period, λ

The kinetic parameters A, U and λ are found to be the function of temperature, t as shown in Eq. 15-17. When these three kinetic parameters are directly used in the modified Gompertz model, the temperature effect term, t automatically get introduced in this equation. Thus the modified Gompertz equation gets reformed with the temperature effect. After introducing the temperature term in the modified Gompertz equation the following equation for lignocellulosic biomass mixed with cattle dung is obtained.

$$P = 2.0264 \times e^{0.0541 \times t} \exp\{-\exp[\frac{0.0845 \times e^{0.0519 \times t} e}{2.0264 \times e^{0.0541 \times t}}(17.512 \times e^{-0.016 \times t} - HRT) + 1]\} \qquad (5.18)$$

where

t = temperature in the range 40°C to 55°C

HRT = hydraulic retention time, 1 to 50 days

Biomasses considered = bamboo dust, saw dust, sugarcane bagasse and rice straw.

Volume of feedstock slurry = 900 ml

Biomass: cattle dung =1:3

Total solid = 9%.

A, U and λ can be calculated using Eq. 15-17, within the range 40°C to 55°C and can be directly applied in Eq. (5.18) to obtain the expected amount of biogas generation from the above mentioned biomass for hydraulic retention time of 50 days with total solid of substrate being 9%. The lignocellulosic biomass considered in this work are bamboo dust, saw dust, sugarcane bagasse, rice straw and rice husk each mixed with cattle dung in 1:3 ratio.

In the similar manner, it is seen that in case of cattle dung too, temperature plays a very important role in determination of kinetic parameters which eventually affects the biogas generation as shown in Table 5.2. Mean of kinetic parameters A, U and λ are plotted against temperature separately and curve fitting is done. It is observed that for temperature between 40°C to 55°C, the kinetic parameters A, U and λ follows an exponential form of order as shown in Eq. 5.19 to 5.21.

$$A = 2.4429 \times e^{0.0502 \times t} \qquad (5.19)$$

$$U = 0.0375 \times e^{0.0674 \times t} \quad (5.20)$$

$$\lambda = 12.943 \times e^{-0.016 \times t} \quad (5.21)$$

Putting the Eq. 5.19, 5.20 and 5.21 in the modified Gompertz equation, a reformed form of an equation for cattle dung is obtained as shown in Eq. 5.22.

$$P = 2.4429 \times e^{0.0502 \times t} \exp\{-\exp[\frac{0.0375 \times e^{0.0674 \times t} \times e}{2.4429 \times e^{0.0502 \times t}} \times (12.943 \times e^{-0.016 \times t} - HRT) + 1]\} \quad (5.22)$$

Eq. (5.22) represents the reformed modified Gompertz model for pure cattle dung.

where

t = temperature in the range 40°C to 55°C

HRT = hydraulic retention time, 1 to 55 days

Substrate = cattle dung

Volume of feedstock slurry = 900 ml

Biomass: cattle dung =1:3

Total solid = 9%

5.5 VALIDATION OF THE REFORMED MODIFIED GOMPERTZ MODEL

5.5.1 VALIDATION FOR CATTLE DUNG WITH PRESENT WORK

It is observed from the present data that cumulative biogas production first decreases with increase in temperature from 35°C to 40°C. After that with increase in temperature from 40°C to 55°C net biogas production increases exponentially. Fig. 5.20 and 5.21 shows the comparison of new model data and experimental data from temperature 35°C to 55°C and from 40°C to 55°C respectively. It is observed that when experimental data from temperature range 35°C to 55°C is compared with the model data the coefficient of regression, R^2 value is found to be 0.811 whereas when temperature 40°C to 55°C is considered R^2 value is found to be 0.891. Therefore the temperature range of the new model is considered to be valid from 40°C to 55°C.

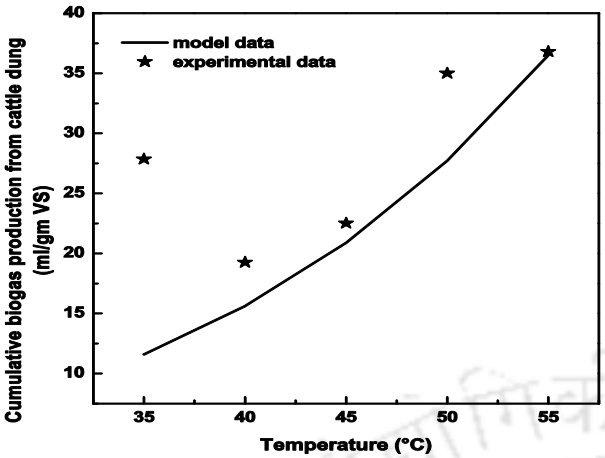


Fig. 5.20 Comparison of model data with present work at temperatures 35°C to 55°C

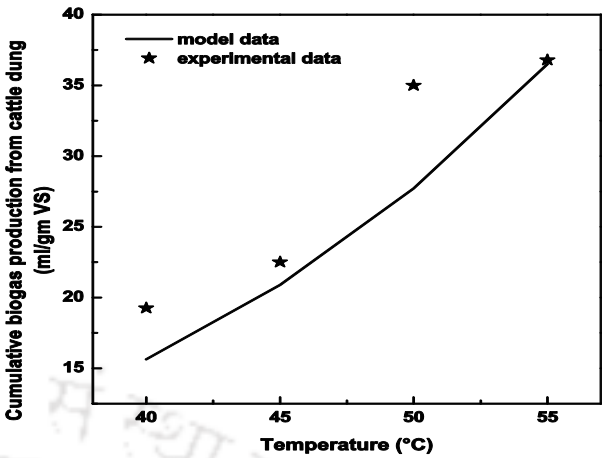


Fig. 5.21 Comparison of model data with present work at temperatures 40°C to 55°C

5.5.2 VALIDATION FOR CATTLE DUNG WITH LITERATURE

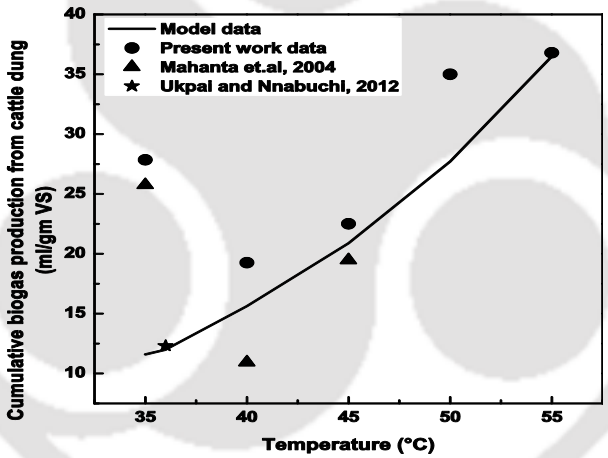


Fig. 5.22 Validation of reformed modified Gompertz model for cattle dung with Literature

Fig. 5.22 shows the comparison of model data, literature data as well as present work data of experiment on biogas production from cattle dung. It is observed that the results of present work as well as literature match quite well with the model data which validate the reformed modified Gompertz model. The percentage variation calculated between kinetic rate constant obtained from the kinetic parameter of modified Gompertz model (maximum biogas production rate, U ml/g/day) at 35°C in present study and literature [Abdullahi et al., 2011] is found to be 8.8% which is pretty low as compared to that of first order kinetic model (22.5%) and literature [Abdullahi et al., 2011].

5.5.3 VALIDATION FOR LIGNOCELLULOSIC BIOMASS WITH PRESENT STUDY

Literature on biogas production from saw dust, bamboo dust, sugarcane bagasse, rice straw and rice husk mixed with cattle dung obeying the conditions of present study is hardly found. So, the validation of reformed form of the modified Gompertz model for lignocellulosic biomass mixed with cattle dung is done with the data obtained from the present study as shown in Fig. 5.23. It is observed that the model conform to the experimental data of biogas production from lignocellulosic biomasses mixed with cattle dung.

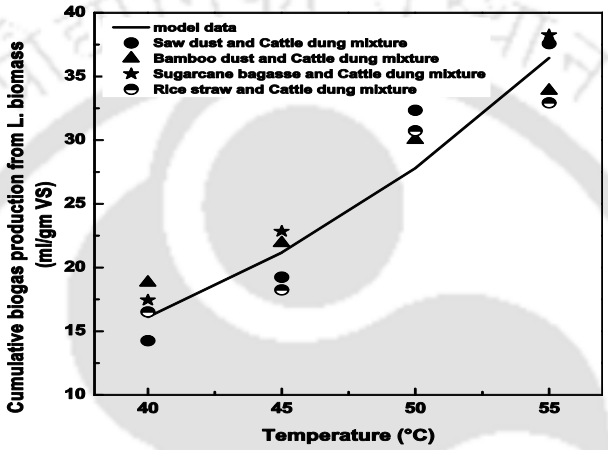


Fig. 5.23 Validation of reformed modified Gompertz model for lignocellulosic biomass mixed with cattle dung with present study

5.6 SUMMARY

Based on the results of small scale anaerobic digestion as shown in chapter 4, the effect of temperature is introduced in the modified Gompertz equation and the model is further reformed for cattle dung as well as for lignocellulosic biomasses mixed with cattle dung. The reformed modified Gompertz model for cattle dung is validated with the present work data as well as literature data. But in case of the above mentioned lignocellulosic biomasses, literature on biogas production under similar condition at various temperatures is hardly reported. Therefore the results of biogas production from lignocellulosic biomass are validated with data obtained from present study on biogas generation from lignocellulosic biomass mixed with cattle dung at different temperature. Subsequently, chapter 6 discusses the biogas purification method using chemical absorption in fixed bed.

CHAPTER 6

BIOGAS PURIFICATION BY CHEMICAL ABSORPTION

6.1 INTRODUCTION

Biogas is a clean renewable energy source for rural India. It mainly consists of methane (55-70%), carbon dioxide (30-45%), hydrogen sulphide (<1%) and some traces of water vapour. Being a non-combustible constituent of biogas, carbon dioxide does not contribute to the combustion; in fact it lowers the heating value of biogas and increases the compression and transportation costs [Mittal, 2006]. So, there is an immense need of removal of carbon dioxide from biogas. Biogas production and subsequent purification will significantly satisfy the fuel requirement in rural as well as urban transport. It provides a clean fuel for both SI (petrol) and CI (diesel) engine. Diesel engines require mixture of biogas and diesel whereas petrol engine can run fully on biogas. For using biogas as vehicle fuel, it has to be purified by removing the impurities like carbon dioxide, hydrogen sulphide and water vapour. These impurities can have detrimental effect on the life cycle and performance of the engine. Removal of carbon dioxide also enhances the calorific value. Therefore it is necessary to purify the biogas before using it for combustion. The purified biogas could be a decentralized source of fuel with uninterrupted supply using cheap and locally available resources. It will generate sufficient opportunities for employment too in rural areas.

6.2 BIOGAS PURIFICATION METHODS

Several researchers have used different types of purification methods as discussed in chapter 2. As observed from the literatures, water scrubbing is a simple, eco-friendly and practical method for carbon dioxide removal from biogas. But it requires a lot of water for this process which makes it impractical for areas with water scarcity. In chemical absorption method, methane concentration at the output decreases rapidly and to maintain high methane concentration frequent replacement of absorbent is needed which makes the operating cost high. Pressure swing adsorption process is very expensive compared to the other methods. If this process is followed, it is essential to remove hydrogen sulphide before removing carbon dioxide which makes it complicated. Membrane separation method has higher operating pressure (25-40 bar), lower methane yield and higher membrane cost. Operating temperature and pressure of

cryogenic separation method is observed to be -100°C and 40 bar, respectively which is very difficult to achieve. The capital as well as operating cost is also very high in this process.

6.3 DESIGN AND DEVELOPMENT OF EXPERIMENTAL SET-UP

Details of the design procedure of the experimental set-up are described in Appendix VI. It is based on the design of canister of carbon dioxide scrubber used in gas mask. The design data are collected from the literature [Nuckols et al., 1985].

Sodalime is used as the absorbent in the designed scrubber to absorb carbon dioxide from biogas. The particle diameter of sodalime granules are measured using electron microscope [make: carl zeiss] and its mean value is found to be 3.75 mm. The design parameters of the scrubber are shown in Table 6.1.

Table 6.1 Design parameters of the scrubber

Design Parameters	Value
Inner diameter of scrubber (D)	120 mm
Length of the scrubber (L)	200 mm
Gas flow rate in the scrubber (Q)	3.28 lpm

Figures 6.1 to 6.4 present various parts of the scrubber like flange, tube, diffuser plate, etc. and Figs. 6.5 and 6.6 shows the scrubber after assembling the parts in horizontal and vertical position respectively.

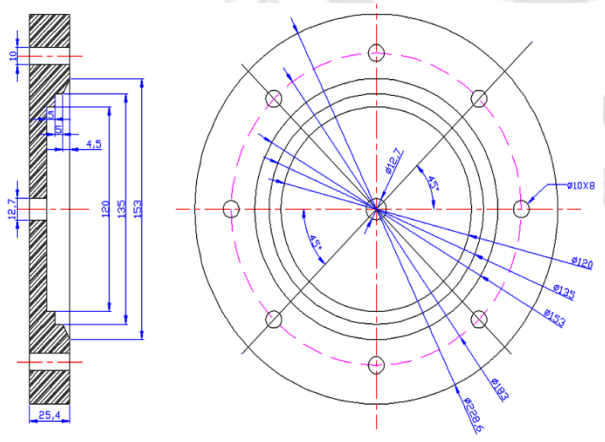


Fig. 6.1 Left flange of the scrubber

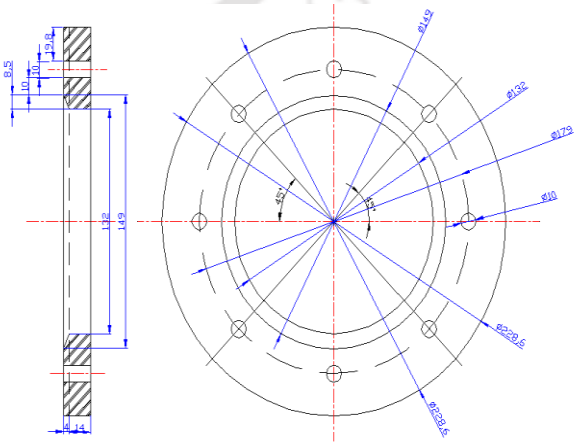


Fig. 6.2 Right flange of the scrubber

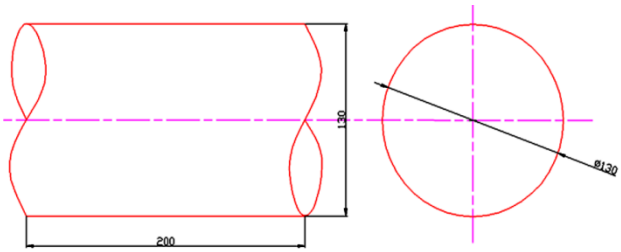


Fig. 6.3 Acrylic pipe of the scrubber

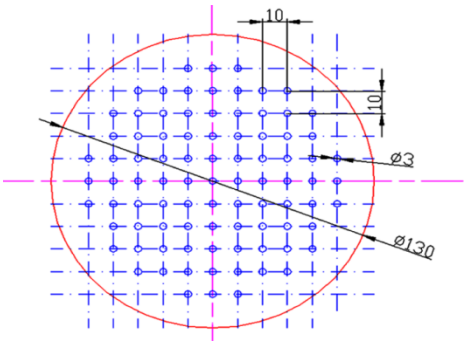


Fig. 6.4 Diffuser plate of the scrubber

Fig. 6.5 The scrubber after assembing (vertical position)

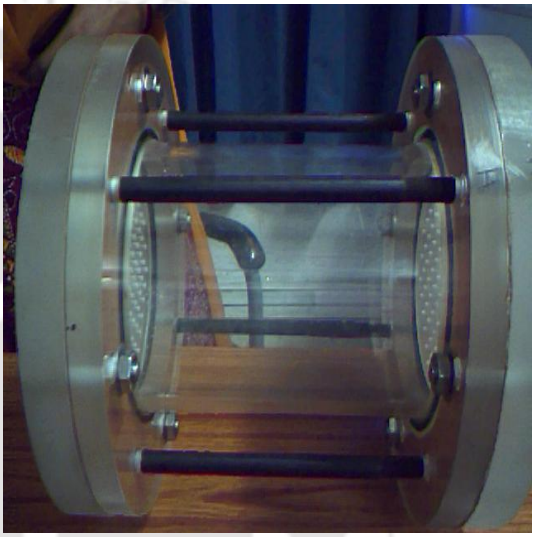


Fig. 6.6 The scrubber after assembing (Horizontal position)

6.4 MATERIALS AND METHODS

It is observed from the literature that the chemical absorption method uses aqueous chemical solution (NaOH solution, amine solution etc.) as the absorbent. However it is difficult to handle because of their corrosive nature. The precipitates of aqueous chemical solution formed at the bottom of the scrubber reduce the performance of the system. Hence it is necessary to use the chemical in dry state to avoid the difficulty faced in this method by aqueous solution. So, it is proposed to use dry chemical in chemical absorption method for purification of biogas. It is supposed to make the system simple and easy to use while avoiding the disadvantages of using aqueous solution of chemicals. Hence sodalime is used as absorbent in chemical absorption method. It is a mixture of chemicals such as $Ca(OH)_2$, NaOH, KOH and some moisture. It is

used worldwide in various applications like anesthesia, respiratory care, hyperbaric chambers, military and tourist submarines, underwater diving gear, fire safety apparatus, mine rescue equipment, etc. [Nuckols et al., 1985]. The most important thing about this chemical is that it is available in the form of pellet, which makes it convenient for easy recharging/discharging. Table 6.2 presents the typical composition of sodalime.

Table 6.2 Typical composition of sodalime [Schon, 2012]

Compositions	**(%)**
$Ca(OH)_2$	94
H_2O	14-19
NaOH	2-4
KOH	1-3%.

The chemical reaction between sodalime and carbon dioxide is an exothermic reaction and it generates humidity [Nuckols et al., 1985]. The temperature rise during the exothermic reaction throughout the scrubber is analogous to a moving temperature front. As the gas passes through the scrubber containing sodalime, carbon dioxide is absorbed by the first layer of sodalime granules and once the sodalime get saturated the reaction proceeds to the next layer of sodalime [Olutoye and Eterigho, 2005].

The reaction between sodalime and CO_2 is a three step exothermic reaction producing water vapour. Equation 6.1 describes how gaseous CO_2 dissolves in water, which is the first of the three step reaction (Reid et al., 1987; Cunningham et al., 2013).

$$CO_2 + H_2O \rightleftharpoons CO_2\,(aq) \qquad (6.1)$$

The second step of the reaction is shown by Eq. 6.2. This shows that the strong base, NaOH is not consumed here rather it acts as a catalyst in the reaction. Due to the high pH this bicarbonate is formed.

$$CO_2\,(aq) + NaOH \rightleftharpoons NaHCO_3 \qquad (6.2)$$

The third and the final step is shown by Eq. 6.3. It deals with the production of calcium carbonates.

$$NaHCO_3 + Ca(OH)_2 \rightleftharpoons CaCO_3 + H_2O + NaOH \qquad (6.3)$$

Combining Eq. 6.1-6.3, the overall reaction can be shown by Eq. 6.4. Heat release in the reaction is found to be 16.4 kcal/mol of CO_2 [W.R. Grace and Co., 1986].

$$CO_2 + Ca(OH)_2 \rightleftharpoons CaCO_3 + H_2O + \Delta H \qquad (6.4)$$

To initiate the CO_2 absorption processes water is required as shown by Eq. 6.1. However in the second step of the reaction water is produced as a by-product of the chemical reaction that takes place within the scrubber (Eq. 6.2). The water required to initiate the absorption process may be furnished by the vapour present in the carrier gas stream.

Sodalime absorbent has been used for over sixty years as a carbon dioxide absorbent for various applications as mentioned above [Nuckols et al., 1985]. But literature is hardly found regarding the use of sodalime to remove carbon dioxide from biogas. In the present work a carbon dioxide scrubber is designed and developed where sodalime is packed as absorbent.

6.5 EXPERIMENTAL SET-UP AND PROCEDURE

Figure 6.7 represents the schematic diagram of the biogas purification system. It consists of a ½ HP air compressor, a 5 lpm capacity rotameter, scrubber, water displacement system and connecting pipes. The raw biogas is compressed and stored in the air compressor and then it is allowed to flow through the scrubber at various inlet gas pressures through the rotameter. Rotameter is a device in which the flow enters the bottom of a vertically placed tapered tube and causes the bob to move upwards. The bob will rise to a point in the tube where the drag force (upward direction) and buoyant force (upward direction) is balanced by the weight of the bob (downward direction). The position of the bob is taken as the indication of the flow rate. It is also called variable area orifice meter as the elevation of the bob is dependent on the annular area between it and the tapered glass tube. Flow rate of the compressed gas passing through the rotameter is controlled with the help of the valves fitted. The gas going out of the scrubber is measured using water displacement system and collected for gas analysis using gas chromatograph (GC).

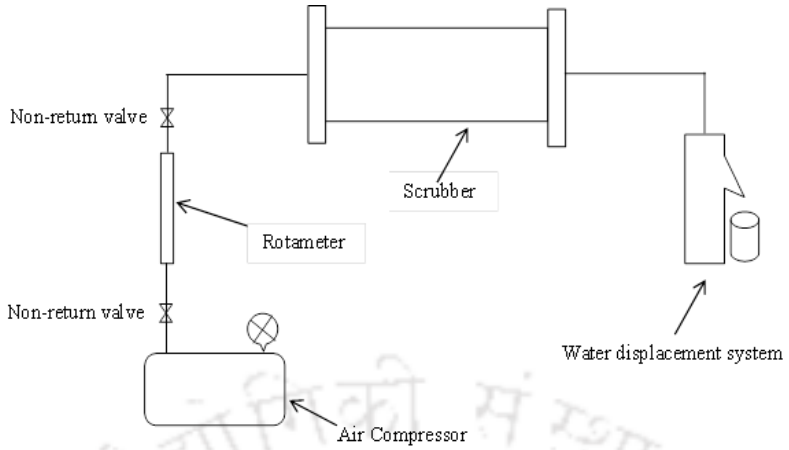


Fig. 6.7 Schematic diagram of the biogas purification system

Raw biogas is first compressed using the single stage air compressor as shown in Fig. 6.8 and then the compressed biogas is allowed to pass through the scrubber at different inlet gas pressure and inlet gas flow rate. K-type thermocouples were fitted to the scrubber at various locations to detect the temperature rise during chemical reaction as shown in Fig. 6.9. Calibration of thermocouple is shown in Appendix VII. Fig. 6.10 shows the water displacement system consisting of brine solution in the solution bottle where the outlet gas is allowed to enter which leads to displacement of the solution. The displaced solution is collected in a beaker. The amount of solution collected directly indicates the amount of gas coming out of the scrubber. The quality of biogas before and after scrubbing was collected in tedler bags and analyzed using gas chromatograph (GC). The gas pressure and flow rate is measured with the help of the pressure gauge and the rotameter fitted to the experimental set-up as shown in Figs. 6.11 and 6.12.

Fig. 6.8 Compression of biogas

Fig. 6.9 Biogas passed through the scrubber

Fig. 6.10 Measurement of purified biogas

Fig. 6.11 Experimental set-up (horizontal)

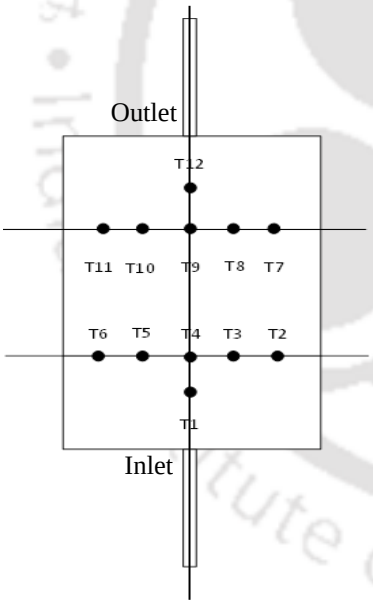
Fig. 6.12 Experimental set-up (vertical)

6.6 RESULTS AND DSCUSSION

6.6.1 TEMPERATURE DISTRIBUTION IN SCRUBBER

Parameters affecting the performance of carbon dioxide scrubber are geometry, wall temperature, inlet gas flow rate, inlet pressure, granule size and material used. The absorption of carbon dioxide by sodalime involves exothermic reaction. The temperature rise during reaction indicates the absorption of carbon dioxide. The transient temperature rise throughout the scrubber is measured with the help of thermocouple placed at various locations within the scrubber. Relationship between reaction and temperature is utilized to give an indication of absorption of carbon dioxide inside the scrubber. As biogas consisting of methane and carbon

dioxide comes in contact with sodalime, chemical reaction occurs and as a result temperature inside the scrubber rises layer by layer. Once the chemical get saturated with the carbon dioxide, the chemical reaction stops and temperature no more increases and starts declining slowly. Twelve k-type thermo-couple were fitted to the carbon dioxide scrubber radially and centrally to study the temperature distribution of the scrubber during biogas flow though the unit. Radially five thermocouples were fitted each in upper and lower plane respectively. The planes were assumed at distance of 40 mm and 160 mm from inlet port. In both the plane thermocouples were fitted at the center and at a distance of 20 mm and 40 mm in either side of the center. Centrally four thermocouples were fitted and they were placed at a distance of 40 mm, 80 mm, 120 mm and 160 mm respectively from inlet port. As biogas enters the scrubber, it gets distributed through the distributor plate. First it hits the thermocouple placed nearest to the inlet port i.e. at 40 mm from inlet port. The temperature rise upto 80°C indicates proceeding of chemical reaction. Figs. 6.13 show the locations of thermocouple fitted in the scrubber.



Thermocouple	Positions
T1 (centre)	40 mm from inlet
T4 (centre, lower plane)	80 mm from inlet
T9 (centre, upper plane)	120 mm from inlet
T12 (centre)	160 mm from inlet
T5 (lower plane)	20 mm from centre
T6 (lower plane)	40 mm from centre
T3 (lower plane)	20 mm from centre
T2 (lower plane)	40 mm from centre
T10 (upper plane)	20 mm from centre
T11 (upper plane)	40 mm from centre
T8 (upper plane)	20 mm from centre
T7 (upper plane)	40 mm from centre

Fig. 6.13 Thermocouple positions in the scrubber

Figure 6.14 presents the central temperature distribution in the carbon dioxide scrubber from the inlet port to the outlet port. As the compressed biogas passes through the chemical in the scrubber the chemical reacts with the carbon dioxide present in the biogas producing heat and moisture along with the product $CaCO_3$. As a result temperature raises upto 80°C. Once the reaction is over, temperature stops rising and the chemical starts cooling naturally, thus the

temperature declines. Figures 6.15 and 6.16 show the radial temperature distribution in upper and lower plane, respectively.

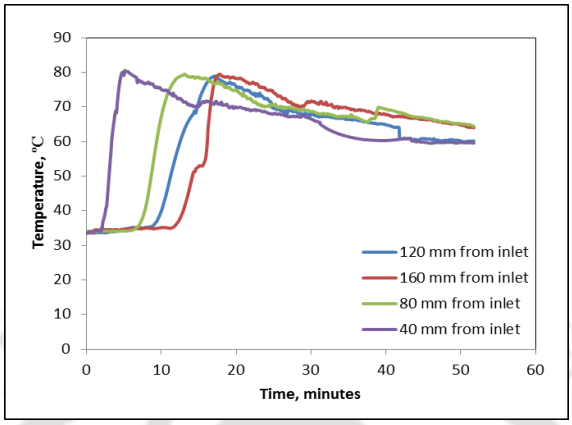


Fig. 6.14 Central temperature distribution from inlet to outlet

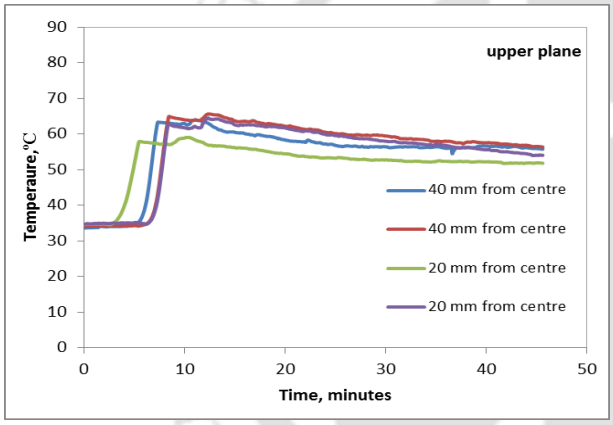


Fig. 6.15 Radial temperature distribution in upper plane

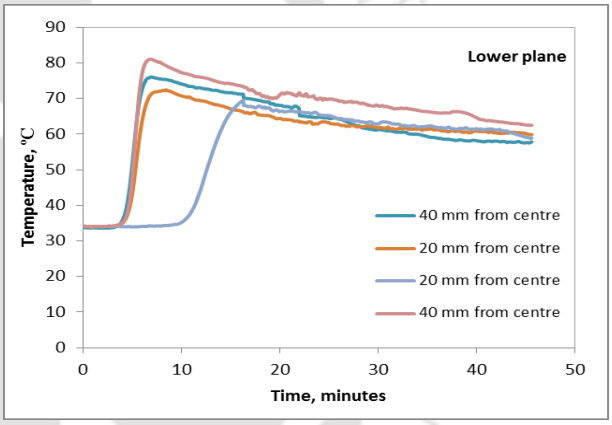


Fig. 6.16 Radial temperature distribution in lower plane

6.6.2 METHANE ENRICHMENT

In this experiment raw biogas is compressed and stored in the air compressor. The compressed biogas is allowed to pass through the scrubber by varying the inlet pressure from 1 bar to 5 bar at an interval of 1 bar with the help of the pressure regulator. The gas flow rate of the inlet biogas is also varied from 1 lpm to 5 lpm at a step of 1 lpm with the help of the rotameter. The raw biogas as well as purified gas coming out of the scrubber is tested for composition analysis with the help of Gas Chromatography (GC). The percentage of carbon di-oxide in the raw biogas was found to be 41.5%. It is observed from Fig. 6.17 and Table 6.3 that with increase in inlet pressure, percentage of carbon dioxide at the outlet gas decreases and with increase in inlet gas flow rate,

percentage of carbon dioxide at the outlet gas increases in case of vertical scrubber. It is observed that inlet pressure of 1 to 3 bar carbon dioxide percentage in the outlet turns out to be more than 5% irrespective of flow rate. Whereas at inlet pressure of 4 and 5 bar the percentage of carbon dioxide in the outlet is found to be less than 5% at all the above mentioned flow rate.

At gas flow rate of 1 lpm, percentage of carbon dioxide content is found to be 2.8% at a pressure of 4 bar whereas at 5 bar it become 1.344%. With increase in inlet pressure from 1 to 4, carbon di-oxide absorption increases considerably. However absorption of carbon dioxide with further increase in inlet pressure from 4 to 5 bar is not found to be quite significant.

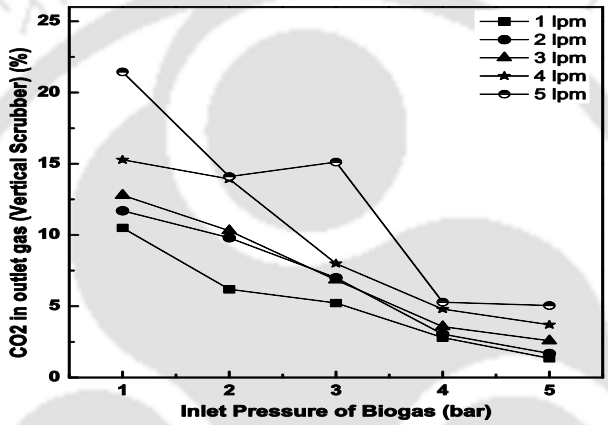


Fig. 6.17 Percentage of CO_2 in purified biogas using vertical scrubber

Table 6.3 Percentages of CO_2 in Biogas after purification with vertical scrubber

Flow rate (lpm) / Inlet Pressure (bar)	**1**	**2**	**3**	**4**	**5**
1	10.5	11.7	12.79	15.28	21.44
2	6.19	9.8	10.3	13.93	14.1
3	5.23	7.0	6.85	8.0	15.12
4	2.8	3.05	3.57	4.8	5.29
5	1.344	1.68	2.57	3.7	5.05

Max. CO_2 concentration in outlet biogas

Min. CO_2 concentration in outlet biogas

Similar is the case with horizontal scrubber as shown in Fig. 6.18. With increase in inlet pressure and decrease in inlet flow rate of biogas, carbon dioxide absorption by soda lime increases for the horizontal scrubber. It is also observed that although the trend of carbon dioxide absorption is almost same for both horizontal as well as vertical scrubber but it is found to be better in case of vertical scrubber as compared to horizontal one. The reason may be due to the effect of gravity which helps in retaining the biogas inside the scrubber for more time in case of vertical scrubber as compared to that of horizontal scrubber.

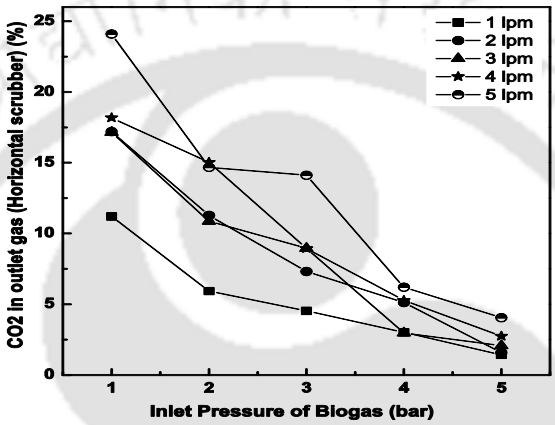


Fig. 6.18 Percentage of CO_2 in purified biogas using horizontal scrubber

6.7 COMPARISON OF RESULTS OF HORIZONTAL AND VERTICAL SCRUBBERS

Figures 6.19 (a) to (e) represent the comparative results of biogas purification obtained from horizontal and vertical scrubbers at gas flow rate of 1 lpm to 5 lpm at an interval of 1 lpm. It is observed that for both of the horizontal and vertical scrubber the minimum carbon dioxide percentage at the purified biogas is obtained at inlet pressure of 5 bar. It is also noticed that with increase in inlet pressure of biogas methane enrichment improves irrespective of gas flow rate. At inlet pressure of 3, 4 and 5 bar and gas flow rate of 1 lpm the carbon dioxide percentage at the outlet is found to be below 5% for both horizontal and vertical scrubber. Whereas with increase in gas flow rates the carbon dioxide percentage in outlet biogas increases for both horizontal and vertical scrubber. This is due to the fact that with increase in flow rate the biogas gets little time to complete the chemical reaction happening between sodalime and carbon dioxide. As a result carbon dioxide present in biogas does not get enough time to get absorbed during the process.

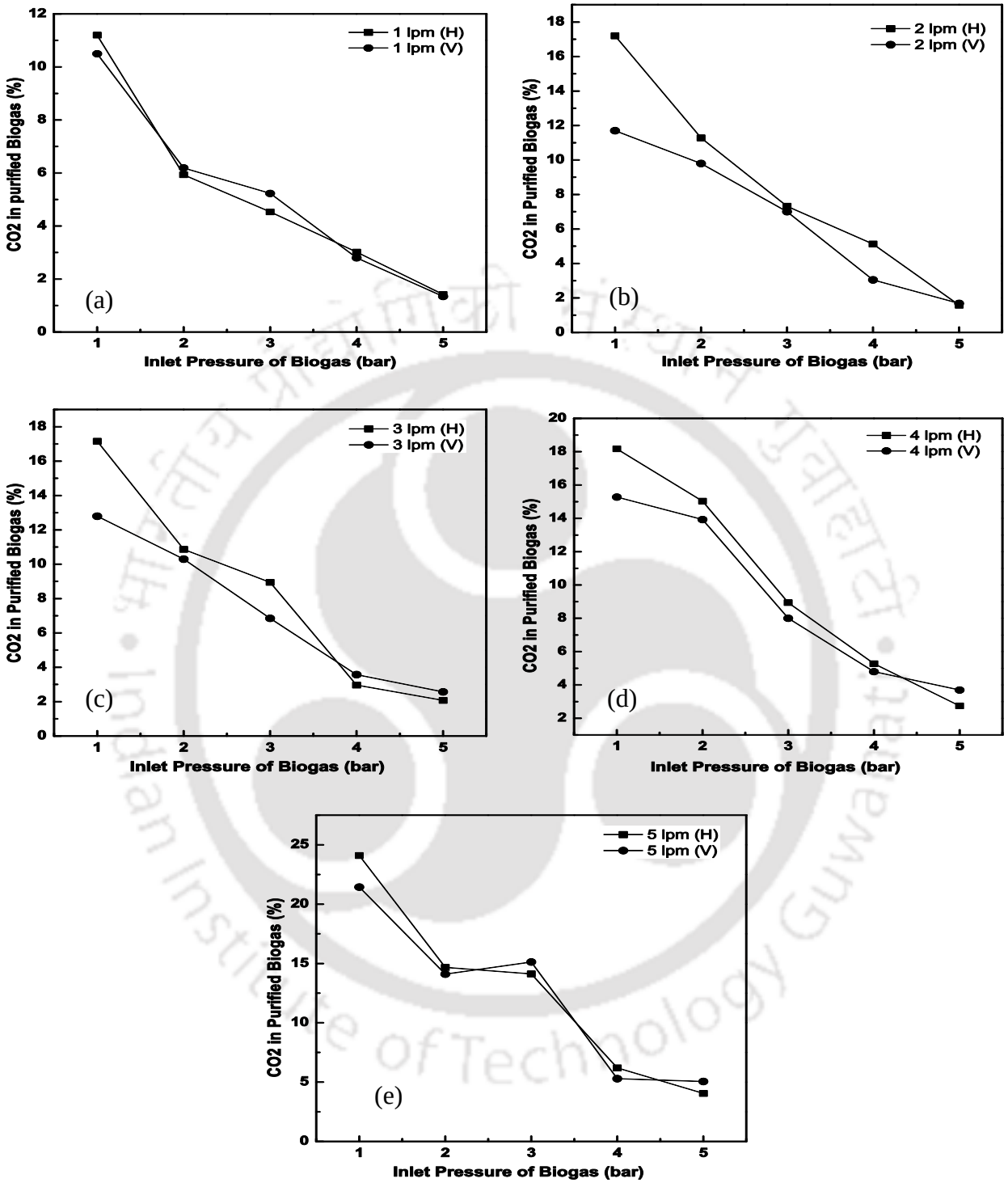


Fig. 6.19 Comparison of results obtained from horizontal and vertical scrubber at (a) 1 lpm, (b) 2 lpm, (c) 3 lpm, (d) 4 lpm and (e) 5 lpm

For inlet pressure of 4 and 5 bar, percentage of carbon dioxide in the outlet for a vertical scrubber is found to be less than 5% at the gas flow rates 1 to 5 lpm, whereas for horizontal scrubber the percentage of carbon dioxide in the outlet is more than 5% under the same condition. Similarly at inlet pressure of 1 to 3 bar, carbon dioxide percentage in outlet is found to be 0.7 to 5.5% higher in case of horizontal scrubber as compared to vertical scrubber at all the gas flow rate considered. The reason can be attributed to the fact that in case of vertical scrubber the gas flow needs to be moved against the gravity which helps the gas in retaining inside the scrubber for more time as compared to that of horizontal scrubber. As a result carbon dioxide absorption in vertical scrubber gets enough time to be accomplished.

6.8 COMPARISON OF RESULTS OF BIOGAS ENRICHMENT WITH LITERATURE

Table 6.4 presents the results of biogas purification using different methods by various researchers along with the results of present work. It is observed that upto 97.7% methane and 1.34% carbon dioxide can be achieved using the present experimental set-up which is quite comparable with literature. Also this method of biogas purification using dry chemical (sodalime) is found to be very effective in rural areas due to the simple design, easy handling of the chemical, and requirement of low pressure and low flow rate of input biogas.

Table 6.4 Comparison of results of biogas enrichment with literature

Sl. No.	Literature	Method	Results
1	Vijay, 2007	Water Scrubbing	99% pure biogas at 1.5 m^3/h gas flow rate and 1.0 MPa gas pressure
2	Ofori-Boateng and Kwofie, 2009		93% pure biogas at1.0 MPa gas pressure
3	Biswas et al., 1977	Chemical Scrubbing (aq. Solution of MEA)	CO_2 content of the biogas was reduced from 40 to 0.5-1.0% by vol.
4	Tippayawong and Thanompongchart, 2010	Chemical Scrubbing (aq. Solution of NaOH)	95.5% methane and 3.2% CO_2
5		Chemical Scrubbing (aq. Solution of $Ca(OH)_2$	95% methane and 4% CO_2
6		Chemical Scrubbing (aq. Solution of MEA)	98% methane and 1.3% CO_2
7	Present study	Dry chemical scrubbing using sodalime	97.7% methane and 1.34% CO_2

6.9 SUMMARY

Although there are various methods of biogas purification available, all of them are not quite acceptable in the rural areas. Most of them are costly and are difficult to handle. Among them the chemical absorption is found to be easier. But due to the use of aqueous solution of chemicals, this method is difficult to handle. That is why the chemical absorption process with dry chemical as carbon dioxide absorber is used in the present study using sodalime as the absorber. The maximum methane content in the purified biogas is found to be 97.7%. Being a high efficiency process with high reaction rates and ability to operate at low pressure this method of biogas purification can surely be used in industrial as well as domestic applications. Chapter 7 reviews the results obtained from the experimental study discussed in previous chapters and evaluate the conclusions and scope for the future work.

CHAPTER 7

CONCLUSIONS AND SCOPE FOR FUTURE WORK

7.1 INTRODUCTION

The rate of consumption of fossil fuels by far has exceeded the rate of their formation which has propelled researchers to look for an environment friendly, cost effective alternative source of energy. Renewable energy sources like lignocellulosic biomass have emerged as wonderful options because they are limitless and they are found to be quite unused source of energy. Also a large volume of lignocellulosic biomasses are generating from agricultural field, crop mills etc., in most of the developing countries like India, china, etc. So, the present work is aimed at investigating the effectiveness and the performance characteristics of anaerobic digestion of lignocellulosic biomass for biogas production.

On the other hand purification of biogas is essential to be used as transport fuel. Because presence of carbon dioxide, hydrogen sulphide and water vapour in biogas have detrimental effect on compression system e.g. corrosion, erosion, fouling etc. Also, presence of carbon dioxide in biogas lowers its calorific value which makes it necessary to purify the biogas before using it. So, the present study is also focused towards the process development to obtain enriched methane from biogas.

7.2 CONTRIBUTION OF THE PRESENT WORK

Based on the characterization done on various lignocellulosic biomasses, five lignocellulosic biomasses were selected and studied for its potentiality for biogas production. They are found to have fairly good amount of cellulose content in it although they contain lignin too. Hence, in the present study effect of various parameters on biogas production are analysed to find out the optimum performance of the lignocellulosic biomass. The parameters considered for the analysis are particle size of biomass, TS of substrate, temperature of substrate, agitation and addition of biochar to cattle dung in appropriate proportion. Kinetic study on biogas production from selected lignocellulosic biomass is carried out at different temperatures using first order kinetic model as well as modified Gompertz model. Based on the results of kinetic study, modified

Gompertz model is reformed. The result of this study will act as a baseline data for biogas production from lignocellulosic biomass, to be followed.

Moreover, biogas purification is studied using chemical absorption method where sodalime is used as medium in fixed bed. This method is found to be advantageous in many aspects as compared to other biogas purification method available.

7.2.1 CHARACTERIZATION OF BIOMASS

To accomplish the aim and objective of the present work fifteen different types of lignocellulosic biomass along with cattle dung are characterized in chapter 3. It is observed from the proximate analysis that TS of rice husk, bamboo dust, sugarcane bagasse, rice straw, newspaper, falling dry leaves, elephant grass, saw dust, dry banana leaves, cattle dung (sundried) and tea-waste ranges from 85-90%. Whereas for Gulmohar leaves and switch grass it ranges from 29-34% and for banana pulp and banana green leaves it ranges from 16-17%. The moisture content of biomass affecting the heating value of the biomass is found to vary from 10-15% in case of gulmohar leaves, banana green leaves, banana pulp and switch grass. The ash content of biomass is the non-volatile inorganic matter which remains after subjecting it to a high decomposition temperature. It is found to vary from 0.5-13% for all the above mentioned biomasses. Volatile matter content of gulmohar leaves, banana green leaves, banana pulp and switch grass is found to be in the range of 2-9% whereas for rest of the biomasses it is in the range of 56-74%. Fixed carbon content is found to be more than 10% for all the biomasses. The consequence of the volatile matter and fixed carbon is that they are responsible for how easily the biomass can be dissolved.

Ultimate analysis of the lignocellulosic biomass have shown that for all the fifteen biomasses considered for the characterization study, the nitrogen content of the biomass is found to be in the range of 0.3 to 2% whereas the carbon content of the biomasses ranges from 10 to 70% which makes the C:N ratio very high. High C:N of substrate is not favourable for optimum biogas production. That is why the biomasses are mixed with cattle dung in 1:3 ratio to adjust the C:N of the substrate for better biogas production. Fibre analysis of the biomasses indicate that except dry tree leaves and elephant grass, lignin content of all the biomasses are found to be in the range of 12 to 30% which is quite high.

7.2.2 PARAMETRIC STUDY ON LIGNOCELLULOSIC BIOMASS

The effect of particle size, TS, temperature, agitation and addition of biochar to the substrate on biogas production is studied in chapter 4. These results suggest that biomass with particle size of 0.355 mm mixed with cattle dung produces highest amount of biogas followed by biomass with particle size of 0.5 mm and 0.85 mm, respectively irrespective of TS content. Also, biogas production from biomass with particle size of 0.355 mm mixed with cattle dung started earlier as compared to biomass of particle size 0.85 mm and 0.5 mm mixed with cattle dung. TS content also affects the biogas production from substrate. When TS of the substrate is 8-9%, highest biogas production can be achieved as compared to 12% and 6% TS of substrate. It is also observed that temperature plays a very important role in biogas production from substrate. Biogas production is found to be the highest at 55°C for all the biomass considered for the parametric study as well as for pure cattle dung. Biogas production at 50°C by the biomass as well as pure cattle dung is also quite good which is near to biogas production at 55°C. Third highest biogas production is obtained at 35°C. Biogas production at 40°C and 45°C is not found to be satisfactory.

It is also observed that agitation of the digestate has improved the biogas production from cattle dung by 69% as compared to without agitation. Also cattle dung mixed with 5% biochar has produced the highest amount of biogas followed by cattle dung mixed with 2.5% biochar and cattle dung with no biochar. Whereas cattle dung with 10% biochar has not produced significant amount of biogas.

7.2.3 KINETIC STUDY OF BIOMETHANATION PROCESSES

Application of first order kinetic model as well as modified Gompertz model to biogas production from lignocellulosic biomass mixed with cattle dung at five different temperatures is studied in chapter 5. The modified Gompertz model easily simulates the biogas production from biomass mixed with cattle dung in mesophilic as well as thermophilic condition, but effect of temperature of biogas generation cannot be evaluated using this model. So, a relation between the kinetic parameter obtained from the modified Gompertz model and temperature is established and implemented in the modified Gompertz equation. Thus, the temperature effect is introduced in the modified Gompertz equation and reformed for better use in future.

7.2.4 BIOGAS PURIFICATION USING CHEMICAL ABSORPTION METHOD

In chapter 6, design and development of carbon dioxide scrubber is done. Biogas purification using sodalime in the scrubber is investigated and found that the present study can reduce the carbon dioxide content of biogas upto 97.7%. The method is found to be simple and easy to use as compared to the other biogas purification methods discussed in the literature.

7.3 SCOPE FOR FUTURE WORK

Based on the extensive parametric study on biogas production from selective lignocellulosic biomass mixed with cattle dung in the present work, kinetic study on biogas production is carried out. Biogas purification using sodalime as medium is also carried out to study the methane enrichment process. However, there remain still numerous scopes for future study, related to this field, which can further enrich the area of lignocellulosic biomass as alternative fuel. These are listed below.

- ❖ In the present investigation, biogas production from lignocellulosic biomass mixed with cattle dung is studied in small scale laboratory set-ups. So in future the same experiment can be repeated for medium as well as for large scale studies and a relationship can be developed among the biogas production in small, medium and large scale.
- ❖ A single correlation can be developed to see the effect of temperature, effect of stirring, effect of particle size, effect of total solid, effect of adding additives etc. on biogas production from biomass.
- ❖ In the reformed modified Gompertz model, effect of stirring, effect of particle size, effect of total solid, effect of adding additives etc. can be introduced to further modify it.
- ❖ The biogas purification is studied using chemical absorption method taking sodalime as medium in fixed bed; in future the same experiment can be repeated in fluidized bed.

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Appendix – I

Characterization of Biomass

I.1 Sample calculations for proximate analysis

Total solids in biomass

Total solid (%) for rice husk = $\frac{1.8313-0.156}{2}\times 100$

$=83.765\%$

where

Weight of dry pan + dry sample is 1.8313 gm

Weight of dry pan is 0.156 gm

Weight of sample as received is 2 gm

Moisture content

Moisture content in husk powder (%) $=100-\frac{1.8313\text{-}0.156}{2}\times 100$

Moisture content in husk powder (%) = 16.235%

Volatile content in husk powder

Volatile content in husk powder $=\frac{m_2-m_3}{m_2-m_1}\times 100$

Volatile content in husk powder $=\frac{57.56439-56.7403}{57.56439-56.55819}\times 100$

Volatile content for husk powder $=81.92\%$

where m_1 = mass of the empty crucible with the lid is 56.55819gm.

m_2=mass of the crucible with lid and the sample before heating is 57.56439 gm.

m_3 = mass of the crucible with lid and the sample after heating is 56.7403 gm.

Ash content in biomass

% of Ash in rice husk powder = $(33.229 - 33.1234) \times 100$

$= 10.56\%$

where

Weight of crucible + rice husk powder is 33.229 gm

Weight of crucible is 33.1234 gm

Weight of sample as received is 1 gm

COD analysis

Sample calculation: Taking concentrations of the sample as 0.025 gm for mixture

A=13 ml

B= 7.2ml

$$M=\frac{20\times 0.2500}{7.2}$$

$$M = 0.6944$$

$$Y = 0.025mg$$

$$X_1 = 5ml$$

$$X = 3.7mg$$

$$V=\frac{5\times 0.025}{3.7}$$

V= 0.0337 ml

$$\text{COD in mg/l}= \frac{(13- 7.2) \times 0.6944\times 8000}{0.03378}$$

COD in mg/l=953878 mg/l

CV analysis

C_v = Heat of combustion of the biomass sample, MJ/kg

W_c = Water equivalent of the bomb calorimeter, MJ/$^{\circ}$C =10.74×10^{-3} MJ/$^{\circ}$C

Initial water temperature = 26.04°C

Final water temperature = 26.87 $^{\circ}$C

ΔT = Rise in temperature, $^{\circ}$C = 0.83 $^{\circ}$C

M_s = Mass of the biomass sample burnt, kg =0.503 gm

$$C_v = \frac{W_c \times \Delta T}{M_s}$$

$$= \frac{10.73 \times 10^{-3} \times (26.87 - 26.04)}{0.503 \times 10^{-3}}$$

$$= 17.699 MJ / kg$$

Table I.1 Characterzation results of lgnocellulosic biomass

Sl. No.	Sample	TS (%)	M (%)	Fixed Carbon	Ash (%)	VM (%)	PH	CV (MJ/Kg)	COD (mg/L)
1	Bamboo Dust	88.23	11.76	12.70	3.79	84.24	7.71	16.75	26476.80
2	Sugarcane Baggasse	86.17	13.82	12.19	1.68	84.17	7.85	18.46	4688.83
3	Rice Husk	89.41	10.59	9.93	14.98	74.07	8.95	14.27	37836.67
4	saw Dust	86.77	13.23	19.98	3.51	82.79	7.28	14.33	37022.41
5	News Paper	89.63	10.36	9.93	7.1	81.81	8.53	11.72	19986.17
6	Rice Straw	87.33	12.66	13.03	19.93	65.15	8.61	13.73	9292.12
7	Elephant Grass	88.51	11.49	12.86	14.48	77.55	7.61	17.69	11802.26
8	Gulmohar leaves	29.43	70.56	19.35	5.38	70.04	6.61	13.60	17738.9
9	Banana leaves (green)	17.05	82.95	12.26	13.73	14.36	6.96	14.89	9514.17
10	Banana leaves (dry)	88.99	11.01	8.27	14.3	76.38	8.9	16.69	27835.70
11	Tree leaves (dry, fallen)	87.15	12.84	15.11	7.15	75.51	7.7	21.43	13975.03
12	Banana Pulp	16.75	83.24	13.46	3.18	16.52	5.44	15.22	60172.63
13	Banana Peel	17.62	82.38	17.62	4.8	78	5.76	16.12	23526.64
14	Switch Grass	34.83	65.16	26.13	8.22	16.73	5.31	15.02	10212.09
15	Tea-Waste	85.55	14.44	7.76	5.54	83.64	6.25	16.87	37573.71
`16	Cattle Dung	19.03	80.96	6.55	22.0	66.2	8.22	14.67	40020.21

Table-I.2 The proximate and ultimate analysis of various lignocellulosic biomass (literature)

Biomass type	Ultimate analysis (db, % w/w)					Proximate analysis (% w/w)				LHV
	C	H	O	N	S	ASH	VM	FC	M	(MJ/kg)
Wood sawdust (Cao et al., 2006)	46.2	5.1	35.4	1.5	0.06	1.3	70.4	17.9	10.4	18.81
Rice husk (Ve´ lez et al., 2009)	45.8	6.0	47.9	0.3	---	0.8	73.8	13.1	12.3	13.36
Rice straw (Li et al., 2009)	38.61	4.28	37.16	1.08	0.65	12.64	65.23	16.55	5.58	14.40
Pine sawdust (Lv et al., 2004)	50.54	7.08	41.11	0.15	0.57	0.55	82.29	17.16	DB	20.54
Spruce wood pellet (Miccio et al., 2009)	49.30	5.9	44.4	0.1	---	0.3	74.2	17.1	8.4	18.5
Coffee husk (Ve´ lez et al., 2009)	46.80	4.9	47.1	0.6	0.6	1.0	74.3	14.3	10.4	16.54
Jute stick (Asadullah et al., 2004)	49.79	6.02	41.37	0.19	0.05	0.62	76-78	21.4-23.4	DB	19.66
Sugar cane bagasse (Asadullah et al., 2004)	48.58	5.97	38.94	0.2	0.05	1.26	67-70	28.74-30.74	DB	19.05
Wheat straw (Oesch, 1996)	46.1	5.6	41.7	0.5	0.08	6.1	75.8	18.1		17.20
Cotton stem (Guo et al., 2001)	42.8	5.3	38.5	1.0	0.2	4.3	72.3	15.5	7.9	15.20
Straw (Shen et al., 2008)	36.57	4.91	40.7	0.57	0.14	8.61	64.98	17.91	8.5	14.60
Camphor wood (Zhou et al., 2009)	43.43	4.84	38.53	0.32	0.1	0.49	72.47	14.75	12.29	17.48
Beech wood (Radmanesh et al., 2006)	48.27	6.36	45.2	0.14	---	0.8	81	18	DB	19.20

VM: Volatile matter, FC: Fixed Carbon, M: Moisture, DB:Dry basis

3.2 Fibre analysis results

Table I.3 Results obtained from the fibre analysis of the feed material

Sl. No.	Biomass	Hemicellulose (%)	Cellulose (%)	Lignin (%)	Lignin to Cellulose ratio
1	Elephant grass	37	32	5.6	0.175
2	Rice straw	35	30.2	22	0.728
3	News paper	36	48	21	0.438
4	Rice husk	24	28	25	0.893
5	Saw dust	2	51	30.1	0.590
6	Bamboo dust	3.8	50	8.2	0.164
7	Sugarcane Bagasse	32.2	41	18.5	0.451
8	Switch grass	44.5	29	13.5	0.466
9	Dry fallen leaves	11	20	15	0.750
10	Banana peel	32.3	58.3	12.2	0.209
11	Tea waste	31.08	30.05	28.56	0.950
12	Cattle dung	12	25	4.5	0.180

Appendix – II

Control of C:N ratio and TS of substrates

II.1 Sample calculation for TS% of biomass and cattle dung mixture with water

Total solid of Bamboo dust=88.235%

Total solid of cattle dung=19.036%

Cattle dung is mixed with biomass in 1:3 ratio.

Total solid of bamboo dust and cattle dung mixture, $TS\% = \frac{88.235 + 3 \times 19.036}{4}$

$=36.34\%$

When water is added to the mixture in 1:2 ratio, $TS\% = = \frac{36.34}{3}$

$=12.11\%$

When water is added to the mixture in 1:3 ratio, $TS\% = \frac{36.34}{4}$

$=9.08\%$

When water is added to the mixture in 1:5 ratio, $TS\% = \frac{36.34}{6}$

$=6.06\%$

Table II.1 TS (%) of biomass before and after mixing with cattle dung and water

Biomass	TS (%)	Biomass+Cattle dung in 1:3 ratio	TS (%)	Biomass+Cattle dung : Water	TS (%) for 1:2 ratio	TS (%) for 1:3 ratio	TS (%) for 1:5 ratio
Bamboo Dust (BD)	88.24	BD+CD	36.34	BD+CD+Water	12.11	9.08	6.06
Sugarcane Bagasse (SB)	86.18	SB+CD	35.82	SB+CD+Water	11.94	8.96	5.97
Rice Husk (RH)	89.41	RH+CD	36.63	RH+CD+Water	12.21	9.16	6.10
Saw Dust (SD)	86.77	SD+CD	35.97	SD+CD+Water	11.99	8.99	5.99
Rice Straw (RS)	87.34	RS+CD	36.11	RS+CD+Water	12.04	9.03	6.02
Cattle Dung (CD)	19.04	TS=12.69 (CD:water=1:0.5); TS=8.95 (CD:water= 1:1.125); TS=6.34 (CD:water=1:2)					

Appendix – III

List of Equipment/Instrument Used

List of instruments used

- Data acquisition system, Agilent 34970A (Data acquisition switch unit with multiplexer)
- Compressor: Capacity: 225 litres, Maximum working pressure: 12.30 kg/cm^2, run by a 3 hp motor, manufacture by Ingersoll Rand (IR), Model: S-01480
- Weighing balance: weighing scale panel, measuring range; max = 15 kg, min = 0.04 kg, error, error =2 gm, Model: SP/p1s-15-FLP, manufactured by Shyaam Switchgears Pvt. Ltd.
- Gas analyzer
- Pressure guage, Make: Swagelok, Model: EN837-1
- Pressure regulator, Make: Swagelok
- Indian standard sieve for particle size measurement (manufactured by Scientific Engineering Corporation)
- Stop watch, Ball valve, Gate valve, Flow control valve, Bye pass valve
- Rotameter for flow measurement: capacity 0 to 5 lpm.
- Thermocouple sensor – type-K
- Thermocouple calibrator with constant temperature bath.

Appendix – IV

Accessories used in the Experimental Set-Up

Fig. IV.1 Water bath where small scale digesters were kept for fermentation under constant temperature condition

Fig. IV.2 Small scale digesters inside water bath kept for fermentation

Accessories used:

1) water baths
2) digesters
3) connecting tube
4) solution bottle
5) conical flask (beaker)
6) copper tube
7) Thermometer
8) measuring cylinder
9) beaker

Fig. IV.3 Various accessories used in the experimental set-up:

Fig. IV.4 Convection Oven

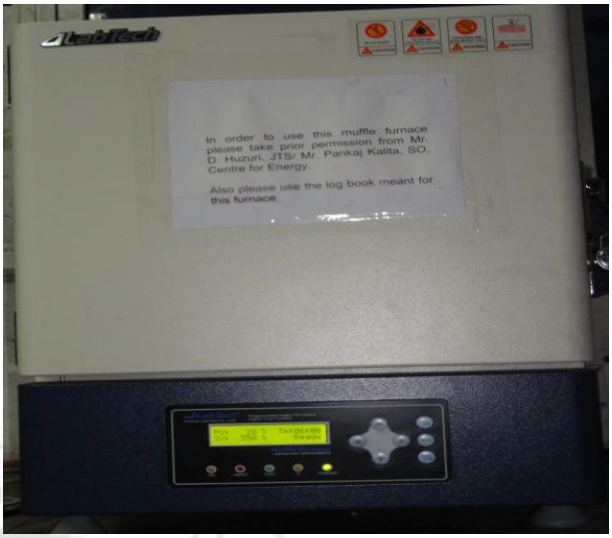

Fig. IV.5 Muffle Furnace

Fig. IV.6 Set-up for COD with heating mantle

Fig. IV.7 Gas Chromatography machine

Fig. IV.8 Laboratory scale digesters

Appendix – V

GC analysis of biogas

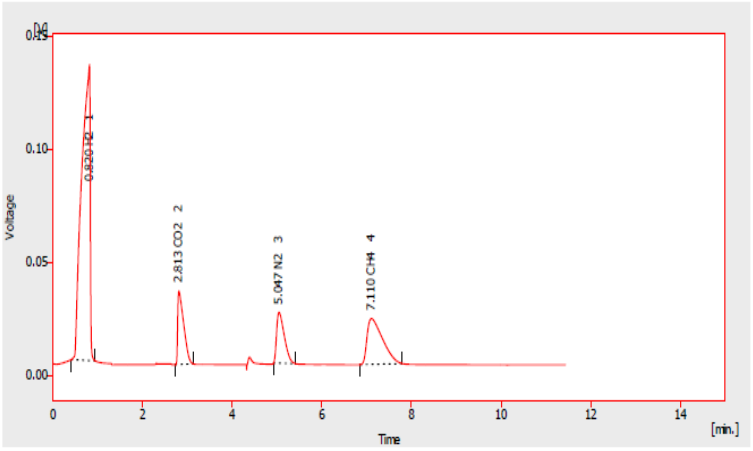

Fig. V.1 GC analysis of biogas from cattle dung

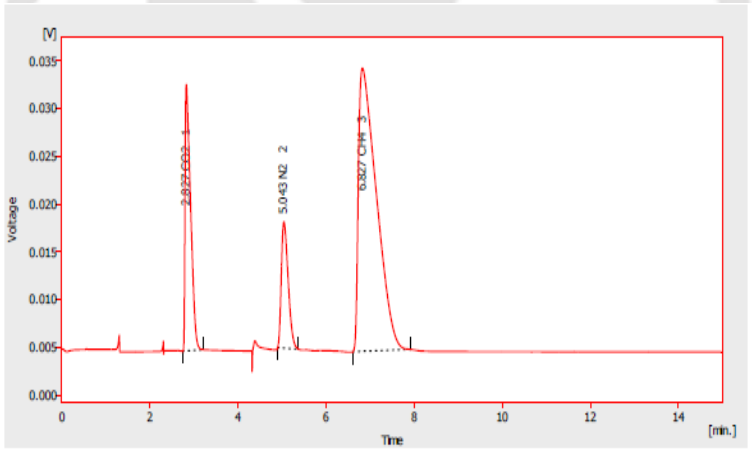

Fig. V.2 GC analysis of biogas from sugarcane bagasse and cattle dung mixture

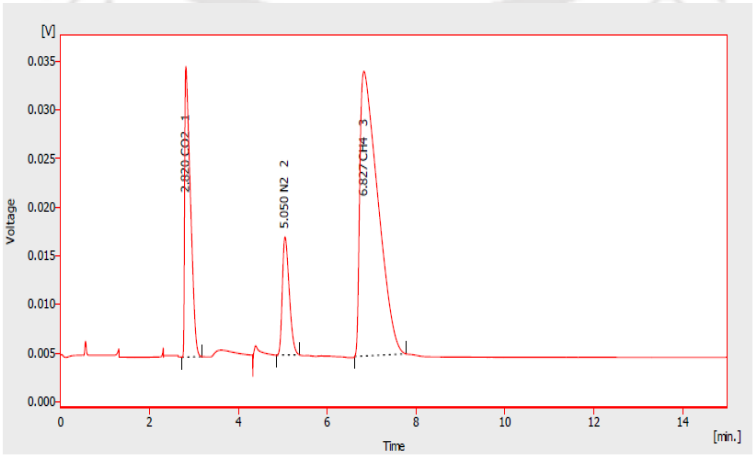

Fig. V.3 GC analysis of biogas from bamboo dust and cattle dung mixture

Appendix – VI

Design and development of carbon dioxide scrubber

Particle diameter of sodalime granules are measured using electron microscope [make: carl zess] and it is found to be 3.75 mm which is well in range [2-5 mm] as per the specification provided by the manufacturer. Thus the mean particle diameter, e = 3.75 mm is considered for the design**.** The design data are taken from literature [Nuckols et al., 1985]

Particle diameter, e varies from 2 to 5 mm. Therefore, considering mean particle diameter,

e = **3.75 mm**

Let us consider **Fig. VI.1** and choosing $\frac{D}{e}$ = 32 where D = diameter of scrubber.

Therefore, **D = 120 mm**.

Now, for 100% canister efficiency **Fig. VI.1** gives particle Reynolds number, $\mathbf{R_e = 1.8}$

From **Fig. VI.2**, for 100% efficiency and 1 atm pressure, $R_e . \left(\frac{L}{D}\right) = 3$

L is the height of the scrubber.

Therefore, **L = 200 mm**.

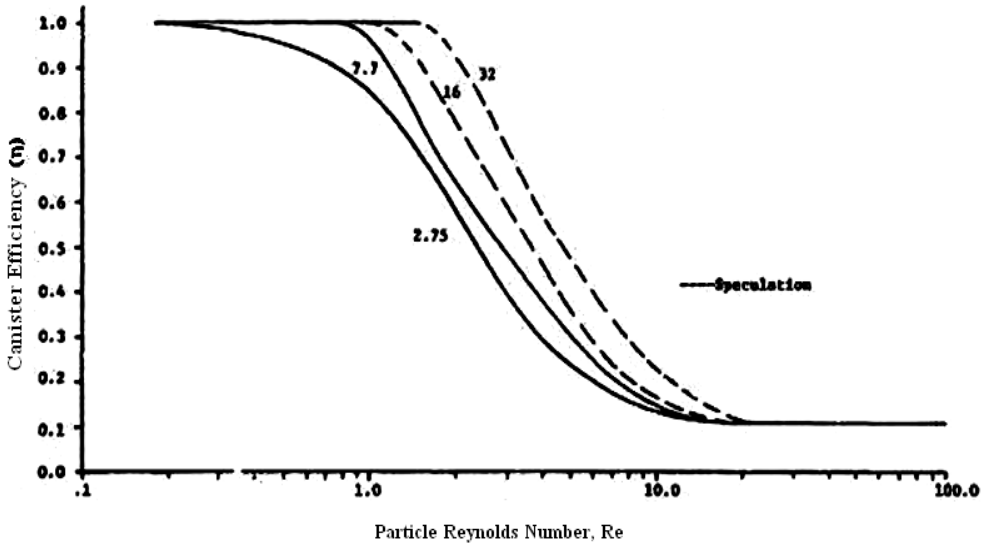

Fig. VI.1 Effect of D/e ratio on canister efficiency[Technical manual by Nuckols et.al, 1985]

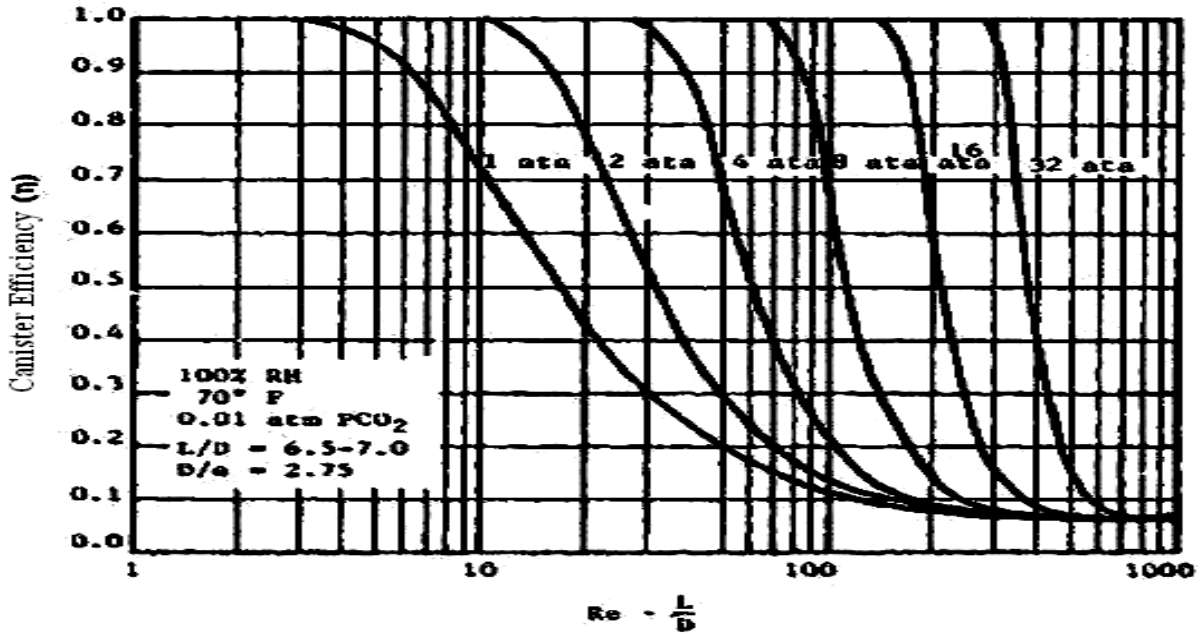

Fig.VI.2 Calculated efficiency of standard test canister at variable pressure [Nuckols et.al, 1985]

To calculate discharge of gas:

We know that, $\mathrm{Re} = \frac{Ve}{\nu}$

where, V is the velocity of flow and ν is the kinematic viscosity of biogas.

For biogas (45% CH_4, 55% CO_2), $\nu = 1.01 \times 10^{-5} m^2 / s$

Therefore, $V = 4.848 \times 10^{-3} m / s$

Now, Discharge, Q = V. $A_{cs,}$ where A_{cs} is the cross sectional area of the scrubber.

$= 4.848 \times 10^{-3} \times \pi \times 0.12 \times 0.12/4$

$= 5.4829 \times 10^{-5} m^3 / s$

= 3.28 lpm

Therefore, the design parameters are, diameter of scrubber, D = 120 mm

Length of scrubber, L = 200 mm

Gas flow rate, Q = 3.28 lpm.

Appendix – VII

Calibration of Thermocouple

The calibration of thermocouple is done by keeping one junction of the two dissimilar metals (Chromel-Alumel) at constant temperature (at 0°C) and other junction is maintained at variable temperatures. In order to maintain variable temperature a water circulating bath is used. A high precision multi-meter is connected in the circuit to see the emf generation. In every 5°C increase of temperature in the water bath emf (millivolt) generation is recorded. The calibration curve so obtained is presented in the Fig.VII.1. Calibration charts were used for high temperature measurement.

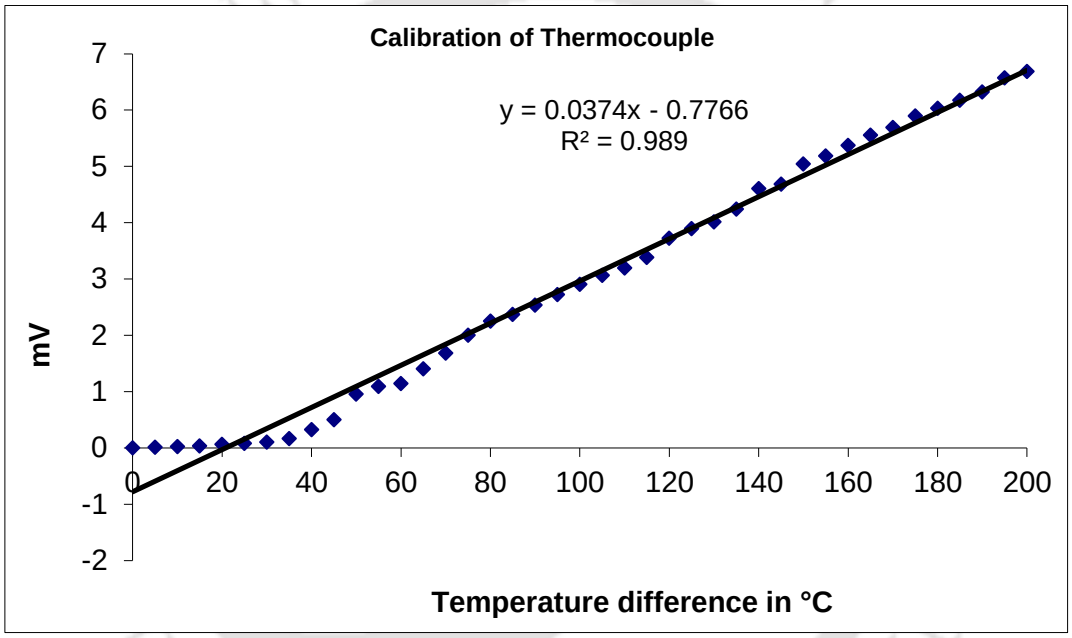

Fig.VII.1 Calibration curve for K-Type thermocouple

List of Publications:

International Journals:

1. **M. Das Ghatak** and P. Mahanta (2014), "Kinetic Assessment of Biogas Production from Lignocellulosic Biomasses". *International Journal of Engineering and Advanced Technology (IJEAT)*, vol. 3(5), pp. 244-249.
2. **M. Das Ghatak** and P. Mahanta (July 2014), "Comparison of Kinetic Models for Biogas Production Rate from Saw Dust", *International Journal of Research in Engineering and Technology*, vol. 3(7), pp. 248-254.
3. **M. Das Ghatak** and P. Mahanta (2014), "The Effect of Temperature and Total Solid on Biomethanation of Sugarcane Bagasse", *The IUP Journal of Mechanical Engineering,* vol.7 (3), pp. 68-75.
4. **M. Das Ghatak** and P. Mahanta (2014), "Effect of Temperature on Co-Digestion of Cattle Dung with Lignocellulosic Biomasses", *Journal of Advanced Engineering Research*, vol. 1(1), pp.1-7 (2014). Received the Best Article Award of 2014.
5. **M. Das Ghatak** and P. Mahanta (2015), "Effect of Temperature on Biogas Production from Rice Straw and Rice Husk" *Journal of Energy in Southern Africa* (communicated).
6. **M. Das Ghatak** and P. Mahanta (2015), "Development of kinetic model for Biogas Production from Lignocellulosic Biomass", *Renewable Energy* (communicated)

International Conferences:

1. **M. Das Ghatak** and P. Mahanta (2013), "Biogas production from lignocellulosic biomasses" Proceedings of the 22nd National and 11th International ISHMT-ASME Heat and Mass Transfer Conference 2013, organized by IIT Kharagpur, India, 28th to 31st Dec'2013.
2. **M. Das Ghatak** and P. Mahanta (2014), "Effect of Temperature on Biogas Production from Lignocellulosic Biomasses", Proceedings of 2014 1st International Conference on Non-Conventional Energy (ICONCE 2014), pp:164-168, organized by JIS College of Engineering, Kalyani, India, 16-17th Jan'2014, Published in IEEE xplore digital library (2014), pp. 117-121. doi:10.1109/ICONCE.2014.6808702.
3. **M. Das Ghatak**, S.K. Mukherjea and B.K. Mandal (2009), "Numerical Prediction of Velocity and Temperature Distributions in a diffusion Flame under Reduced Gravity Conditions", Proceedings of the International Conference on Advances in Mechanical Engineering, pp: 247-251, organised by S.V. National Institute of Technology, Surat, India, August 3-5, 2009.
4. D. Yadav, D. Bora, R. Purkayastha, **M. Das Ghatak**, L. Barbora, P. Mahanta T. Radu, R. Blanchard and A. Wheatley (2014), " Small Scale Anaerobic Digestion: A Case Study", 37th WEDC International Conference, 15–19 September 2014, Hanoi, Vietnam.