A STUDY OF SINGLE STAGE SEMI-DRY ANAEROBIC DIGESTION OF ORGANIC FRACTION OF MUNICIPAL SOLID WASTE

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by

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A Study of Single Stage Semi-Dry Anaerobic Digestion of Organic Fraction of Municipal Solid Waste

Ph.D. Thesis under the Faculty of Engineering

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Certificate

This is to certify that the thesis entitled **"A Study of Single Stage Semi-Dry Anaerobic Digestion of Organic Fraction of Municipal Solid Waste"** is an authentic original work done by **Sajeena Beevi. B** under our supervision and guidance in School of Engineering, Cochin University of Science and Technology. No part of this thesis has been presented for any other degree from any other institution.

We further certify that the corrections and modifications suggested by the audience during the pre-synopsis seminar and recommended by the Doctoral Committee of Sajeena Beevi. B are incorporated in the thesis.

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Declaration

I hereby declare that the work presented in the thesis entitled **"A Study of Single Stage Semi-Dry Anaerobic Digestion of Organic Fraction of Municipal Solid Waste"** is based on the original work done by me under the supervision of Prof. G. Madhu and Prof. Dipak Kumar Sahoo, Division of Safety and Fire Engineering, School of Engineering, Cochin University of Science and Technology. No part of this thesis has been presented for any other degree from any other institution.

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Dedicated to my family…

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Abstract

Solid waste generation is a natural consequence of human activity and is increasing along with population growth, urbanization and industrialization. Improper disposal of the huge amount of solid waste seriously affects the environment and contributes to climate change by the release of greenhouse gases. Practicing anaerobic digestion (AD) for the organic fraction of municipal solid waste (OFMSW) can reduce emissions to environment and thereby alleviate the environmental problems together with production of biogas, an energy source, and digestate, a soil amendment. The amenability of substrate for biogasification varies from substrate to substrate and different environmental and operating conditions such as pH, temperature, type and quality of substrate, mixing, retention time etc. Therefore, the purpose of this research work is to develop feasible semi-dry anaerobic digestion process for the treatment of OFMSW from Kerala, India for potential energy recovery and sustainable waste management. This study was carried out in three phases in order to reach the research purpose.

In the first phase, batch study of anaerobic digestion of OFMSW was carried out for 100 days at 32°C (mesophilic digestion) for varying substrate concentrations. The aim of this study was to obtain the optimal conditions for biogas production using response surface methodology (RSM). The parameters studied were initial pH, substrate concentration and total organic carbon (TOC). The experimental results showed that the linear model terms of initial pH and substrate concentration and the quadratic model terms of the substrate concentration and TOC had significant individual effect ($p < 0.05$) on biogas yield. However, there was no interactive effect between these variables ($p > 0.05$). The optimum conditions for maximizing the biogas yield were a substrate concentration of 99 g/l, an initial pH of 6.5 and TOC of 20.32 g/l. AD of OFMSW with optimized substrate concentration of 99 g/l [Total Solid (TS)-10.5%] is a semi-dry digestion system .Under the

optimized condition, the maximum biogas yield was 53.4 L/kg VS (volatile solid)..

In the second phase, semi-dry anaerobic digestion of organic solid wastes was conducted for 45 days in a lab-scale batch experiment for substrate concentration of 100 g/l (TS-11.2%) for investigating the start-up performances under thermophilic condition (50°C). The performance of the reactor was evaluated by measuring the daily biogas production and calculating the degradation of total solids and the total volatile solids. The biogas yield at the end of the digestion was 52.9 L/kg VS for the substrate concentration of 100 g/l. About 66.7% of volatile solid degradation was obtained during the digestion. A first order model based on the availability of substrate as the limiting factor was used to perform the kinetic studies of batch anaerobic digestion system. The value of reaction rate constant, k, obtained was 0.0249 day^{-1}.

A laboratory bench scale reactor with a capacity of 36.8 litres was designed and fabricated to carry out the continuous anaerobic digestion of OFMSW in the third phase. The purpose of this study was to evaluate the performance of the digester at total solid concentration of 12% (semi-dry) under mesophlic condition (32°C). The digester was operated with different organic loading rates (OLRs) and constant retention time. The performance of the reactor was evaluated using parameters such as pH, volatile fatty acid (VFA), alkalinity, chemical oxygen demand (COD), TOC and ammonia-N as well as biogas yield. During the reactor's start-up period, the process is stable and there is no inhibition occurred and the average biogas production was 14.7 L/day. The reactor was fed in continuous mode with different OLRs (3.1,4.2 and 5.65 kg $VS/m^3/d$) at constant retention time of 30 days. The highest volatile solid degradation of 65.9%, with specific biogas production of 368 L/kg VS fed was achieved with OLR of 3.1 kg $VS/m^3/d$.

Modelling and simulation of anaerobic digestion of OFMSW in continuous operation is done using adapted Anaerobic Digestion Model No 1 (ADM1).The proposed model, which has 34 dynamic state variables, considers both biochemical and physicochemical processes and contains several inhibition factors including three gas components. The number of processes considered is 28. The model is implemented in Matlab® version 7.11.0.584(R2010b). The model based on adapted ADM1 was tested to simulate the behaviour of a bioreactor for the mesophilic anaerobic digestion of OFMSW at OLR of 3.1 kg VS/m^3/d. ADM1 showed acceptable simulating results.

Keywords: Anaerobic digestion; organic fraction of municipal solid wastes; batch study; continuous study; thermophilic; mesophilic; organic loading rate; optimization; response surface methodology; volatile solid degradation; biogas yield; modelling.

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Abbreviations

AD	Anaerobic Digestion
ADM1	Anaerobic Digestion Model Number 1
C/N	Carbon to Nitrogen ratio
CCD	Central Composite Design
COD	Chemical Oxygen Demand
CSTR	Continually Stirred Tank Reactor
DAD	Dry Anaerobic Digestion
DC	Developing Countries
HRT	Hydraulic Retention Time
HS	High Solids
KSUDP	Kerala State Urban Development Project
LCFA	Long Chain Fatty Acid
LFG	Landfill Gases
LS	Low Solids
MC	Moisture Content
MS	Medium Solid
MSW	Municipal Solid Waste
OFMSW	Organic Fraction of Municipal Solid Waste
OLR	Organic Loading Rate
RSM	Response Surface Methodology
RT	Retention Time
SRT	Solids Retention Time
SWM	Solid Waste Management
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TS	Total Solids
UASB	Upflow Anaerobic Sludge Blanket
ULB	Urban Local Bodies
VFA	Volatile Fatty Acids
VS	Volatile Solids

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Chapter 1

INTRODUCTION

Contents

1.1 Background

Rapid population growth, industrialization and urbanization have inflamed the problems associated with management of municipal solid waste (MSW). Ineffective and inappropriate solid waste management is responsible for numerous problems such as environmental pollution, low level of sanitation, unhygienic living conditions etc. The need for a systematic management of an ever increasing trend of MSW generation complicated by complex waste characteristics is a massive challenge for solid waste management. In this regard, the safe, long-term and reliable final waste disposal system has become a major environmental issue in several countries particularly in developing nations. In order to answer this problem, several experts in the field of waste management studied various waste management techniques and control strategies.

The principal methods of managing solid waste include reuse, recycling, composting, incineration and landfilling. Generally, landfilling was the most economical and dependable MSW disposal system being practiced worldwide. Based on the fact that all waste processing methods generates residues that cannot be further reused or recovered, eventually must be landfilled. Nevertheless, it was currently realized that direct landfilling of waste was not an environmentally friendly approach in which various potential risks and hazards associated with landfills could create an imbalance in ecosystem. Such impacts includes emission of landfill gases like methane and carbon dioxide which were known to cause global warming, the generation of leachate that constitute a lasting and detrimental effects on the water environment, the unavailability and diminishing land resources, the energy crisis and the risks associated with landfill stability. Continued open dumping and unsophisticated land filling of solid waste in major cities of developing world will result in significant health and environmental consequences, because, the uncontrolled decomposition of waste could lead to epidemic diseases, proliferation of foul odours and climate change. The existing waste dumping sites are gone beyond their capacity. It is difficult to get new dumping sites and open dumping is prohibited by law. This is particularly true for Kerala, with severe constraints of land availability, dense population and environmental fragility.

Pre-treatment of municipal solid waste prior to landfilling reduces the load to landfill that increases the life of landfill. Pre-treatment of organic fraction of municipal solid waste (OFMSW) by anaerobic digestion was viewed as an integral part in solid waste management, because of its suitable waste characteristics. In India, more than 90 % of the municipal solid waste

generated is dumped in an unsatisfactory way, which creates environmental hazards to water, air and land. At the same time the organic fraction of MSW is about 40-60 % (Mufeed et al., 2008). In Kerala, around 70% of the waste is compostable organics enabling high level of recycling in the form of manure or fuel (Varma & Dileep, 2004).The anaerobic digestion is an attractive option for energy generation from the putrescible fraction of MSW as well as for reducing the disposal problem (Metcalf & Eddy, 2004). It has reduced environmental impact, especially with respect to the greenhouse effect and global warming.

Anaerobic digestion (AD) is a biological process wherein diverse group of microorganism convert the complex organic matter into a simple and stable end product in the absence of oxygen (L.De Baere, 2000). This process is very attractive because it yields biogas, a mixture of methane and carbon dioxide, which can be used as renewable energy resources. AD of OFMSW is used in different regions worldwide to reduce the amount of material being landfilled, stabilize organic material before disposal in order to reduce future environmental impacts from air and water emissions and recover energy. Several research groups have developed anaerobic digestion processes using different organic substrates (Forster-Carneiro et al., 2007a., Gallert et al., 2003., Hansen et al., 2008). In this view, anaerobic digestion of solid waste is a process that is rapidly gaining momentum to new advances especially in the area of dry anaerobic fermentation and has become a major focus of interest in waste management throughout the world. Moreover, when compared to other conversion technologies for treatment of the organic fraction of MSW, the economic, energy, and environmental benefits makes anaerobic digestion an attractive option

(Chynoweth et al., 1994). But, anaerobic digestion process is chemically complex and technically demanding. Number of plants especially in developing countries has failed in solid waste anaerobic digestion because of operational and technical problems. Thus there is a need to develop technologies to address the problems faced during its implementation particularly at large scale.

1.2 Problem Statement

The organic waste is required to be managed in a sustainable way to avoid depletion of natural resources, minimize risk to human health, reduce environmental burdens and maintain an overall balance in the ecosystem. Anaerobic digestion is widely being practiced as major treatment option for disposal of organic municipal solid waste on par with composting technology. Anaerobic digestion mainly combines with the energy recovery benefits, greenhouse gas mitigation and produces stable end products, which can be further upgraded as compost for land application (Forster-Carneiro et al., 2008; Walker et al., 2009). In general, anaerobic digestion systems are broadly categorized under wet (<10 wt% total solids) or dry (>15 wt % total solids), mesophilic (30-40^{o}C) or thermophilic (50-55^{o}C), batch or continuous and single or two stage systems (Fdez-Guelfo et al., 2010; Forster-Carneiro et al., 2008; Yabu et al. 2011).

Several studies have been made on the bioconversion of biomass by different researchers. For example Mata-Alvarez et al. (1992) carried out experiments on Barcelona's central food market organic wastes, Lane (1984) and Prema Viswanath et al.(1992) on fruit and vegetable wastes, Krishna et al.,(1991) on canteen wastes, Ranade et al., (1987) on market

waste etc. There is a large number of factors which affect biogas production efficiency such as environmental conditions like pH, temperature, type and quality of substrate, mixing, process inhibitory parameters like high organic loading, formation of high volatile fatty acids, inadequate alkalinity etc. (Brummeler et al., 2000). Therefore, the amenability of substrate for biogasification, gas yield–organic loading relationships, bioprocess conversion efficiency and process inhibitory parameters vary from substrate to substrate.

Dry anaerobic digestion technology has tremendous application in the future for sustainability of both environment and agriculture because it represents a feasible and effective waste stabilization method to convert the undiluted solid bio-waste into renewable energy with nutrient rich organic fertilizer. When compared with wet anaerobic digestion, dry anaerobic digestion is beneficial to its compact digester with high organic loading rate and its energetically effective performance (Pavan et al., 2000). This process also results in a lower outcome of leachate and easy handling of digested residues that can be further treated by composting process or be used as fertilizer. However, there is limited practice for the application of this process especially in developing countries due to the lack of appropriate treatment system configurations and mainly due to the longer time required for the bio stabilization of waste. To reduce the retention time, semi-dry digestion (TS is between 10% and 15%) can be practiced. Any kind of reactor design and operational criteria selection are depends upon the feedstock characteristics, economical aspects etc. Anyhow, each mode of operation always has its own advantages and limitations.

Therefore, the purpose of this research work is to develop feasible semi-dry anaerobic digestion process for the treatment of OFMSW from Kerala, India for potential energy recovery and sustainable waste management.

1.3. Goal and Objectives of the Study

The main goal of this study is to develop feasible semi-dry anaerobic digestion process for the treatment of OFMSW for potential energy recovery and sustainable waste management. Different research works were carried out with the purpose of achieving the main goal.

The specific objectives of this study are as follows:

- To study the effect of substrate concentration (based on the total solids content in the reactor) on the mesophilic anaerobic digestion of OFMSW in terms of biogas production under batch process.
- To optimize the parameters of anaerobic digestion system mentioned above.
- To describe the kinetics of AD of OFMSW
- To study the performance of batch reactor under thermophilic condition at optimized total solid concentration (semi-dry digestion).
- To evaluate the performance of mesophilic semi-dry anaerobic digester operating in continuous mode by using different OLRs.
- To assess the quality of the digested solids and liquid effluent for their further use.
- To develop a mathematical model for anaerobic digestion of OFMSW in a continuous process.

1.4 Scope of the Study

To accomplish the above objectives, scope of the study is given as follows:

- Organic fraction of MSW (food waste 37%, vegetable waste 35%, fruits waste 25%, and paper 3%) was used as the main feed stock.
- The OFMSW were collected from nearby vegetable market and house hold at Thrissur, Kerala, India.
- The inoculum used in this study was fresh cattle dung.
- Characteristics of waste, inoculums, feed stock and digestate as well as operational parameters of digestion were analysed.
- Experiments were conducted in three phases; mesophilic batch study, thermophilic batch study and bench scale semi -continuous study.
- Performance of the AD process was evaluated in terms of COD, VFA removal, biogas yield and biological activity.
- Batch study was conducted to evaluate the optimum substrate concentration for semi-dry AD system.
- Bench scale reactor was operated under different OLRs of 3.1,4.2 and 5.65 kg VS/m^3/d
- Development of mathematical model for anaerobic digestion of OFMSW in a continuous process.

1.5 Thesis Framework

The thesis is divided into six major chapters. Chapter 1 introduces the statement of research problem and research objectives. The second chapter is devoted for the review of literature. A review of earlier investigations in the related topics is made in this chapter. The materials and methods adopted for the study are presented in chapter 3. The experimental set-up required for the study and various methods for the analysis are also described in this chapter. The results obtained from the experiments are reported and discussed in chapter 4. The fifth chapter describes the dynamic modelling and simulation of anaerobic digestion of OFMSW using adapted ADM1 model. A complete description of ADM1 model is provided in this chapter. General conclusions and scope of the further research are presented in chapter 6. The references are listed at the end.

Chapter 2

LITERATURE REVIEW

Contents

2.1 Introduction

The massive generation of biological wastes is a serious issue in the present scenario. The rapid increase in population, urbanization, industrialization etc. has accelerated the pace of the accumulation of municipal wastes globally. Increasing urbanization and economic development in developing countries have greater impact on management of society's solid wastes. Today, the urban areas of Asia produce about 760,000 tons of MSW per day. In 2025, this figure will increase to 1.8 million tons of waste per day (World Bank, 1999). It is affecting all walks of human life. These estimates are conservative and the real values are probably more than double this amount. The inefficiency in waste management methods causes many hazards like environmental pollution, dreadful diseases etc. The unscientific and improper handling of MSW during its collection, storage and transportation poses

serious environmental and public health effects. Thus an appropriate and effective waste management is inevitable. The waste management method must be a safe and sustainable one such that its negative impact on human beings and the ecosystem is minimal (Guendouz et al., 2010)

The waste disposal methods depend on the nature and characteristics of waste generated. It in turn depends on the features of the locality of generation and the characters of the inhabitants of the locality. So choosing a safe and significant method of waste management is invariably depended on the nature of the region from where it is originated. Since the nature of wastes varies from place to place, the disposal methods by knowing the characteristics of the wastes will be better and efficient (Visvanathan et al., 2004).

Solid waste streams should be characterized by their sources, by the types of wastes produced, as well as by generation rates and composition. Accurate information in these areas is essential in order to monitor and control existing waste management systems and to make regulatory, financial, and institutional decisions. Hence waste characterization is very significant in the field of solid waste management. According to Mufeed sharsholy et al., (2008) waste characterization is normally conducted as a part of waste management studies or environmental impact assessment studies. Waste from all sources must be tested for the following properties: (a) composition; (b) physical properties; (c) chemical properties; (d) biological properties; (e) thermal properties; (f) toxic properties and (g) geotechnical properties. However currently very unhealthy and inappropriate methods of waste disposal like open dumping is practiced in the society. Since the effects of such unscientific methods are devastating man needs to resort on other dependable and non-polluting ways of waste management.

2.2 Municipal Solid Waste Scenario in Kerala

Municipal solid waste (MSW) is a waste type that includes predominantly domestic waste with sometimes the addition of commercial waste collected by a municipality within a given area. The rapid urbanization, constant change in consumption pattern and social behaviour has increased the generation of municipal solid waste in Kerala. Generally, data on the quantity of MSW generation is maintained by the Urban Local Bodies (ULBs). Based on the studies carried out by the Centre for Earth Science Studies and data compiled by the Clean Kerala Mission for all the Municipalities and Corporations of the State, the average daily per capita generation comes to 0.378 kg with a very high variation from 0.034 kg for Koothuparamba to 0.707 kg for Thalassery (Varma & Dileep, 2004). The total MSW generation in the entire state, estimated based on the population figure of 2001 and projected for the year 2006 (Information from Kerala State Urban Development Project, KSUDP, (R. Ajayakumar Varma, 2006) is given in Table 2.1. A portion of the MSW generated will be collected by rag pickers for recycling and reuse.

Table 2.1 Waste Generation scenario in Kerala in 2006
(*Source*: Dr. R. Ajaykumar Varma, 2006)

	Population 2001	Per capita waste generation (g)	Tot Waste generation (t/day)	Projected population 2006	Projected waste generation (g)	Total waste Generation 2006 (t/day)
5 Corporations	2456618	435	1069	2543812	465	1183
53 Municipalities	2731093	250	683	2828030	268	758
999 Panchayats	23574449	175	4126	2441200	187	4565
Total Waste Generation in Kerala			5878			6506

2.3 Composition of Municipal Solid Waste

MSW is a heterogeneous waste, which may be divided into a number of sub fractions:

- Digestible organic fraction. It is also called Organic Fraction of Municipal Solid Waste (OFMSW); which is readily degradable i.e. kitchen waste, grass cuttings, paper, etc.
- Combustible fraction: Slowly digestible and indigestible organic matter i.e. wood, cardboard, plastics and other synthetics etc.
- Inert fraction: Stones, sand, glass, metals, bones etc.

The composition of MSW stream in Asian cities shows high (>50%) biodegradable organic fraction (Visvananthan et al., 2004). However, the composition differs depending on the economic level of cities as well as other factors such as geographic location, energy sources, climate, living standards and cultural habits, and the sources of waste that are considered as MSW or are collected by the municipality.

OFMSW contains typically 40-50% cellulose, 12% hemicellulose, and 10-15% lignin by weight (Wang et al., 2003). The composition of the OFMSW is important in determining which treatment method is most appropriate. In this respect, numerous papers have focused on aspects of anaerobic digestion of biodegradation of the OFMSW according to its origin: e.g., market waste, fruit and vegetable, food waste and kitchen waste (Mata-Alvarez et al., 2000; Kim et al., 2002; Rao et al.,2004) .

Composition of MSW generated in Kerala is described below (Dr. R. Ajayakumar Varma, 2006). The physical composition of MSW is important

for deciding the prime management actions namely the reduction, reuse and recycling of waste. The physical composition of wastes is reported by Varma & Dileep, 2004; which is given in Table 2.2. It indicates that in the major cities of the state, around 70% of the waste is compostable organics enabling high level of recycling in the form of manure or fuel. The chemical characterization of waste is important to understand the utilisation as well as the pollution potential of the waste. The chemical composition of MSW from four major cities of the state as reported by the KSUDP is given in Table 2.3. It indicates high moisture content, low calorific value and high nutrient content making the dominant organic fraction of waste more conducive for recycling in the form of manure.

Table 2.2 Physical composition of MSW from different townships of Kerala (%) (*Source*: Dr. R. Ajayakumar Varma 2006)

Composition	Chenganasseri	Kottayam	Kannur	Aluva	Thiruvananthapuram	Average
Paper	10.20	6.80	8.20	9.72	2.25	7.43
Plastic	4.90	4.25	6.67	6.94	2.79	5.11
Metals	0.20	2.00	1.40	1.38	1.02	1.20
Glass	0.50	2.25	1.60	1.00	1.30	1.33
Rubber & Leather	0.60	2.20	1.67	1.77	2.11	1.67
Compostable organics	76.60	73.45	68.73	70.83	69.09	71.7
Others-Textiles, Inerts & domestic hazardous	7.00	9.05	11.73	8.36	21.44	11.52

Table 2.3 Chemical characteristics of MSW at the dumping sites of major cities of Kerala

Sl No.	Sampling Location/ area	Density (Kg/m^3)	Moisture Content (%)	Calorific Value (kcal/kg)	pH	C (%)	N (%)	C/N	P as $P_2 0_5$
1	Kollam	207.06	74.32	1656	7.72	24.97	0.97	25.74	553.5
2	Kochi	267.81	55.29	1759	7.46	26.39	1.25	21.11	129.25
3	Thrissur	335.50	69.52	1744	7.40	28.68	0.93	30.84	1561.17
4	Kozhikode	327.65	79.54	1816	7.12	32.72	2.43	13.46	1050.17
	Average	284.51	69.67	1744	7.43	28.19	1.40	22.79	823.52

2.4 Energy Potential of Municipal Solid Wastes

The compromise between the energy and the environment is a recent controversial issue. Generally, people assume that energy generation and environmental protection activities contradict each other. More clearly, most of the energy generation systems exploit the natural resources and are a hazard to the environment in terms of source depletion and environmental contamination. One of the solutions of this problem is to implement synergy between environmental protection and energy generation. There are many areas in environmental technologies that facilitate both waste treatment and energy generation in a cycle. Solid waste is one of the typical examples of energy recovery systems. There are various options available to convert solid waste to energy such as incineration, sanitary landfill (landfill gas), gasification, pyrolysis, anaerobic digestion, and others. All these technologies have their own merits and demerits. The choice of the technology should be based on the local and socio-economic conditions as well as waste quality and quantity. Among these AD is one of the most attractive technologies as this technology is comparatively less

expensive than other methods for same energy production. Since methane is a potentially explosive gas and is also a more effective greenhouse gas, it has to be controlled before emitting from landfill. Experiences in many countries of the world show that Landfill Gases (LFGs) can be successfully used to replace other energy sources. According to Braber, (1995) the net electricity production of 100-l50 KWh per tonne of OFMSW is found which shows a large energy potential of OFMSW. Typical composition of biogas is given in Table 2.4.

Table 2.4 Typical biogas composition (Source: RISE-AT, 1998; Braber, 1995)

Energy content	20-25 MJ/m^3
Methane (CH_4)	55-70%
Carbon dioxide (CO_2)	30-45%
Hydrogen sulfide (H_2S)	200-4000 ppm

2.5 Fundamentals of Anaerobic Digestion

Anaerobic digestion is a natural process by which microorganisms break down biodegradable material in the absence of oxygen. AD is considered as an alternative option to manage and treat the organic fraction of municipal solid waste. This process not only treats the organic waste but also produces clean energy (biogas). The digestion residues (digestate) obtained from the process can be used as soil amendment or even nutrient rich organic fertilizer depending on its final quality. There are number of benefits resulting from the use of AD technology which are described in Table 2.5.

Table 2.5 Benefits of anaerobic digestion of MSW

Aspects	Feature of benefits
Waste treatment benefits	Natural waste treatment process
	Requires less land than aerobic composting or landfilling
	Reduces disposed waste volume and weight to be landfill
	Reduces concentrations of leachate
Energy benefits	Net energy producing process
	Generates high quality of renewable fuel
	Biogas proven in enormous end use applications
Environmental benefits	Significant reduction of greenhouse gas emissions
	Eliminate odours
	Produces sanitized compost and nutrient rich fertilizer
	Maximizes recycling benefits
Economic benefits	Cost effective than other treatment options from a life cycle perspective

Disadvantages of AD system

- AD cannot be used to remove nutrients - nitrogen or phosphorous from wastewater.
- Upsets caused by acidification is a common problem and pH control is an important factor in stable operation. The cost of alkali required for pH control can negate all cost advantages of anaerobic treatment.
- AD of MSW does not treat whole waste, only a fraction of it.
- Anaerobic reactors take long time for start-up and, therefore, seeding with quality sludge becomes important.
- Wastewater may need to be treated before disposal.

Generally, the overall AD process of OFMSW can be divided into three stages: pre-treatment, anaerobic digestion process, and post-treatment.

2.5.1 Pre-treatment of Feedstock

Pre-treatment of waste was regarded as the first phase of the overall anaerobic digestion system. The main purpose of pre-treatment is to increase biodegradability thereby, enhances the digestion process. Pre-treatment normally includes (1) physical separation of the organic fraction from inorganic materials; (2) reduction of particle size; (3) the addition of inoculants, leachates or additives into the feedstock; (4) treatment of the substrates with acid, alkali, ultrasonic or thermal energy or their combination before digestion.

Pre-treatment methods for OFMSW can be biological, mechanical or physicochemical (Mata-Alvarez et al., 2000). Biological pre-treatment can be achieved by the means of aerobic pre- composting methods which show positive improvement of methane yields and solids reduction. Miah et al. reported that addition of aerobic thermophilic sludge improves the biogas production and solids reduction, presumably that thermophilic aerobic bacteria secrete external enzymes which dissolve particulate organic matters more actively (Miah et al., 2005).

Mechanical pre-treatment is commonly aimed to reduce particle size. Size reduction, providing a uniform small particle size feedstock for efficient digestion and mixing the waste with other substrates into a desired consistency are often involved. Palmowski and Muller explained that size reduction of the particles and the resulting enlargement of the available specific surface can support the biological process in two ways (e.g. improved

digester gas production and reduction of technical digestion time) and the main advantage of this, was the possibility to harmonize the digestion time in case of a heterogeneous input and to reduce the required digester volume (Palmowski L.M. and Müller, J.A, 2000).

Chemical pre-treatment can be accomplished by alkaline pre-treatment. The chemical treatment of the fibres with NaOH, NH_4OH or a combination led to an increased methane potential (Mata-Alvarez et al., 2000). The same improvement was also reported when a pre-treatment by addition of lime was done (Lopez et.al 2008). Chemical pre-treatment changes the composition of waste by reducing particulate organic matter to soluble form i.e. proteins, fats, carbohydrates or lower molecular weight compounds. Alkalis are added to increase the pH to 8-11 during this process. Thermal and chemical pre-treatments do improve hydrolysis and promote solubilisation.

2.5.2 Microbiological Processes in Anaerobic Digestion

Anaerobic digestion of organics is a complex process, which can be divided into 4 biodegradation stages, with four different types of microorganisms: hydrolysis (hydrolytic bacteria), acidogenesis (acidogens), acetogenesis (acetogens), and methanogenesis (methanogens). The different stages of anaerobic digestion are depicted in Figure 2.1.

1. Hydrolysis

An important step of the anaerobic biodegradation process is the hydrolysis of the complex organic matter. During the anaerobic digestion of complex organic matter, the hydrolysis is the first and often the rate-limiting step (Neves,L et al., 2006). The rate of hydrolysis is a function of pH, temperature, concentration of hydrolytic bacteria, and type of particulate

organic matter and the physicochemical properties of particulate organic substrates.. In this process hydrolytic organisms hydrolyse complex organic matter such as proteins, poly carbonates, lipids, etc. to simple organic compounds (format, acetate, propionate, butyrate and other fatty acids, etc.) (Chaudhary, 2008).

An approximate chemical formula for the mixture of organic waste is $C_6H_{10}O_4$ (Ostrem, 2004). A hydrolysis reaction where organic waste is broken down into a simple sugar (glucose) can be represented by the equation (2.1).

$$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + 2H_2 \quad \text{.....(2.1)}$$

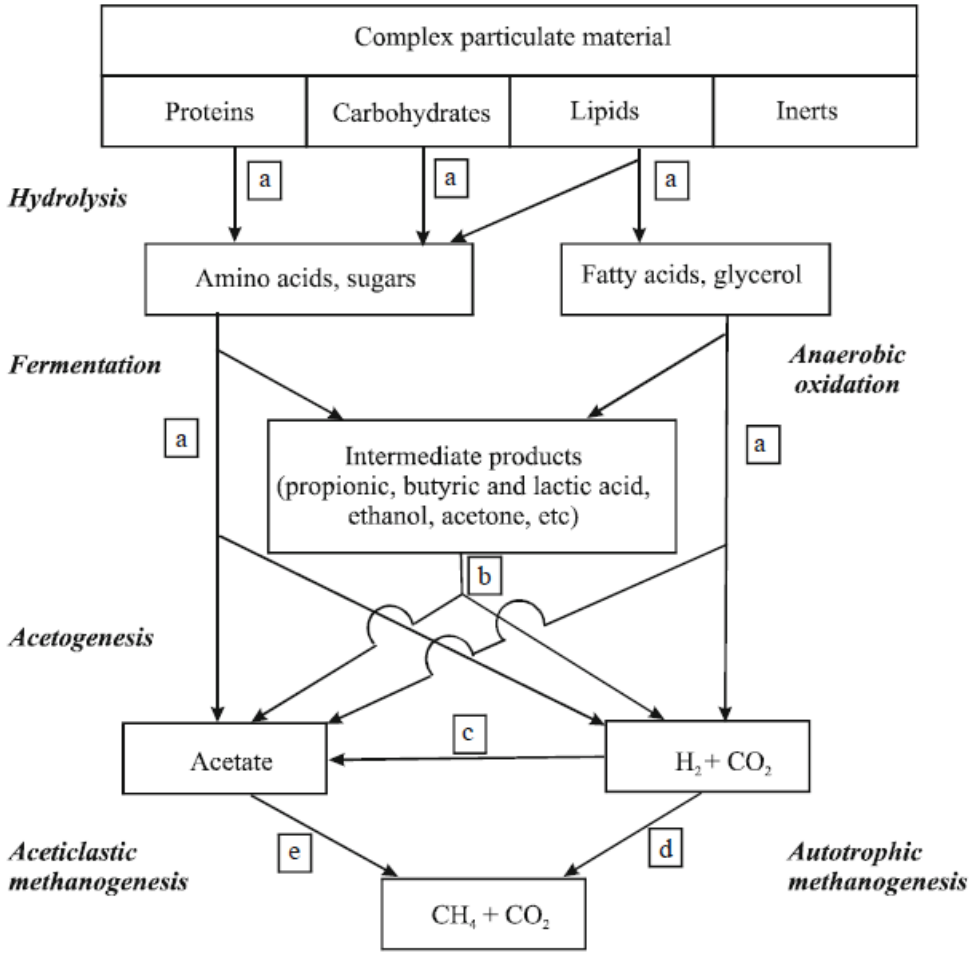
2. Acidogenesis

In this stage, the hydrolysed compounds are fermented into volatile fatty acids (acetic, propionic, butyric, valeric acids etc.), neutral compounds (ethanol, methanol), ammonia, and the pH falls as the levels of these compounds increases. Carbon dioxide and hydrogen are also evolved as a result of the catabolism of carbohydrates. The group of microorganisms responsible for this biological conversion is obligate anaerobes and facultative bacteria, which are often identified in the literature as acidogens.

Typical reactions in the acid-forming stages are shown below. In equation (2.2), glucose is converted to ethanol and eq. (2.3) shows glucose is transformed to propionate.

$$C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2 \text{ ..... (2.2)}$$

$$C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2H_2O \text{ ..... (2.3)}$$



a. Hydrolytic and fermentative bacteria
b. Hydrogen producing acetogenic bacteria
c. Hydrogen consuming acetogenic bacteria
d. Carbon dioxide reducing bacteria
e. Aceticlastic methanogens

Figure 2.1 Anaerobic digestion processes (*source*: Manariotis et al., 2010)

3. Acetogenesis

The third step is acetogenesis where the simple molecules from acidogenesis are further digested to produce carbon dioxide, hydrogen and acetate. This conversion proceeds with the action of obligate hydrogen producing acetogenic bacteria, which are considered as acetogens.

Acetogenesis occurs through carbohydrate fermentation in which acetate is the main product and other metabolic processes also occur. The result is a combination of acetate, CO_2 and H_2. The role of hydrogen as an intermediary is of critical importance to AD reactions. Long chain fatty acids, formed from the hydrolysis of lipids, are oxidized to acetate or propionate and hydrogen gas is formed. Under standard conditions, the presence of hydrogen in the solution inhibits the oxidation. The reaction only proceeds if the hydrogen partial pressure is low enough to thermodynamically allow the conversion. The presence of hydrogen consuming bacteria thus lowers the hydrogen partial pressure, which is necessary to ensure thermodynamic feasibility and thus the conversion of all the acids. As a result, the concentration of hydrogen, measured by partial pressure, is an indicator of the health of a digester (Mata-Alvarez, 2003). The Eq.(2.4) shows the conversion of propionate to acetate.

$$CH_3CH_2COO^- + 3H_2O \leftrightarrow CH_3COO^- + H^+ + HCO_3^- + 3H_2 \ldots\ldots \text{(2.4)}$$

4. Methanogenesis

Methanogenesis is the last stage of anaerobic digestion which involves the production of methane from the raw materials produced in the previous stage. Generally, the methanogenic substrates include acetate, methanol, hydrogen or carbon dioxide, format, methanol, carbon monoxide, methylamines, methyl mercaptans, and reduced metals. Methanogens which carry out the terminal reaction in the anaerobic process are the most important in anaerobic digester systems. The methane is produced from a number of simple substances: acetic acid, methanol or carbon dioxide and hydrogen. Among these, acetic acid and the closely related acetate are the

most important, since around 75% of the methane produced is derived from acetate (Evans G, 2001).

Methanogens can be divided into two groups: acetate consumers that utilize acetic acid known as acetoclastic methanogenesis whereas hydrogen and carbon dioxide utilizing consumers are known as hydrogenotrophic methanogenesis. The growth of methanogens is slower than the bacteria responsible for the preceding stages. This population converts the soluble matter into methane, about two thirds of which is derived from acetate conversion (eq. 2.5) followed by (eq.2.6), or the fermentation of an alcohol, such as methyl alcohol (eq. 2.7), and one third is the result of carbon dioxide reduction by hydrogen (eq. 2.8) (Ostrem, 2004).It has been estimated from stoichiometric relations that about 70% of the methane is produced via the acetate pathway (Metcalf & Eddy, 2003).

$$2CH_3CH_2OH + CO_2 \leftrightarrow 2CH_3COOH + CH_4 \quad \text{..... (2.5)}$$

$$2CH_3COOH + CO_2 \leftrightarrow CH_4 + CO_2 \quad \text{..... (2.6)}$$

$$CH_3OH + H_2 \leftrightarrow CH_4 + H_2O \quad \text{..... (2.7)}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \text{..... (2.8)}$$

2.5.3 Post Treatment of Residual Fraction from AD

After anaerobic digestion is completed, the remaining biodegradable solid waste residues are commonly subjected to post treatment. Such treatment includes dewatering, aeration, and leachate treatment. The purpose of aeration as post treatment is to remove lingering organics, to

aerobically reduce the compounds and to produce valuable products such as fertilizer and soil conditioner. The solid fraction can be matured for about two to four weeks to provide dry and fully stabilized compost. Either the liquid fraction may be recycled for the dilution of fresh waste, applied directly to farmland as a liquid fertilizer, or sent to a wastewater treatment plant. If the MSW is treated in a dry process, the digested material is usually dewatered and matured to compost. Most of the liquor is recycled to moisten and inoculate the incoming raw MSW, but there will usually be a small surplus that can be spread on farmland as a liquid fertilizer, or treated in a wastewater treatment plant. The amount, quality and nature of digestate depend upon the quality of the feedstock to the anaerobic digestion process, the method of digestion, and the extent of the post-treatment refining process. As the digestate can be used as soil conditioner after post treatment, the energy consumption in fertilizer manufacturing could be reduced (Monnet, 2003). Application of digestate or liquor to farmland is dependent on digestate quality and local regulations. The ability to utilize the residues of anaerobic digestion as soil amendments improves the economics and environmental benefits of the AD process.

a). Dewatering of digestate

The digestate usually contains fibre and liquor which has to be separated. There are different methods of dewatering such as screw press, wire presses, centrifuges, decanters and cyclones. The filtered cake is cured aerobically, usually in compost piles, to make compost. The fibre is bulky and contains a low level of plant nutrients so it can be used as soil conditioner. The liquor contains a large proportion of nutrients, which can be used as a fertilizer. Its high moisture content facilitates it

application through conventional irrigation methods. However consideration has to be given to application time so that nitrogen, which is more readily available after digestion, is taken up by the crop and not leached into the soil and subsequently groundwater.

b). Composting of digestate

In order to obtain a high quality product, with a higher value, the digestate can be processed into compost. It would ensure a complete breakdown of the organic components as well as fixing the mineral nitrogen onto humus like fraction, which would reduce nitrogen loss. As an additive to composting process, it provides a good source of nitrogen for seeding up the process. At the same time, it enriches the compost in phosphorus and micro nutrients such as manganese (Mn), iron (Fe) etc. the water content of the digestate is also interesting for maintaining the moisture in the composting process. The compost made from MSW has to meet consumer and market requirements. The following criteria are important to ensure the marketability:

- It must be largely free of impurities
- It must not present any health hazards
- The level of heavy metals and other toxic substances must comply with the standards
- The product must have a visually attractive overall impression

2.6 Factors Affecting Anaerobic Digestion

There are numerous factors affecting the breakdown of organic matter in anaerobic digestion process. The control of several operating parameters

within the digester enhances the microbial activity and improves process efficiency. Several digestion parameters affect the physical system and consequently the rate of digestion and production of biogas. The following parameters must be monitored and maintained at acceptable levels to ensure process stability: substrate characteristics/volatile solids, pH and alkalinity, volatile fatty acid concentration, temperature, carbon to nitrogen (C/N) ratio, hydraulic retention time, organic loading rate, solid retention time, mixing and inhibitory substances. Deviations from the acceptable ranges for these parameters can result in digester failure and it is essential to understand the importance of each parameter.

2.6.1 Substrate Characteristics/Volatile Solids (VS)

The characteristics of solid wastes such as its composition determine the successful anaerobic digestion process (*e.g.* high biogas production potential and degradability).The generation and composition of MSW vary from site to site and are influenced by various factors such as region, climate, and method of collection, season, and cultural habits of community. The wastes treated by AD may comprise a biodegradable organic fraction, a combustible and an inert fraction. The biodegradable organic fraction includes kitchen scraps, food residue, and grass and tree cuttings. The combustible fraction includes slowly degrading lignocellulosic organic matter containing coarser wood, paper, and cardboard. As these lignocellulosic organic materials do not readily degrade under anaerobic conditions, they are better suited for waste-to-energy plants. Finally, the inert fraction contains stones, glass, sand, metal, etc. This fraction ideally should be removed, recycled or used as landfill. The degradability and biogas production potential from solid waste in an anaerobic digester are dependent on the

amount of the main components: lipids, proteins, carbohydrates such as cellulose and hemicelluloses as well as lignin (Hartmann and Ahring, 2006). The composition of wastes affects the yield and biogas quality as well as the compost quality (Verma, 2002).

The volatile solids comprise the Biodegradable Volatile Solids (BVS) fraction and the Refractory Volatile Solids (RVS). Kayhanian and Rich (1995) reported that knowledge of the BVS fraction of MSW helps in better estimation of the biodegradability of waste, of biogas generation, organic loading rate and C/N ratio. Lignin is a complex organic material that is not easily degraded by anaerobic bacteria and constitutes the RVS in organic MSW. Waste characterized by high VS and low non-biodegradable matter is best suited to AD treatment. The composition of wastes affects the yield and biogas quality as well as the compost quality.

2.6.2 pH and Alkalinity

The pH value of the digester content is an important indicator of the performance and the stability of an anaerobic digester. Variation in pH affects the anaerobic digestion because the hydrogen ion concentration has direct influence on microbial growth. It has been determined that an optimum pH value for AD lies between 5.5 and 8.5 (RISE-AT,1998). During digestion, the two processes of acidification and methanogenesis require different pH levels for optimal process control. The ideal pH for methanogens ranges from 6.8 to 7.6, and their growth rate will be greatly reduced below pH 6.6 (Mosey et al., 1989). The optimum pH for hydrolysis and acidogenesis is between 5.5 and 6.5 (Arshad, et al., 2011). The retention time of digestate affects the pH value. Most anaerobic bacteria including

methane forming bacteria function in a pH range of 6.5 to 7.5, but optimally at a pH of 6.8 to 7.6, and the rate of methane production may decrease if the pH is lower than 6.3 or higher than 7.8 (Stronach et al., 1986; Lay et al., 1998).

The alkalinity is a measure of the capacity of the solution to neutralize acids. Optimal anaerobic biotechnology is characterized by nearly neutral conditions. Process imbalance can be due to low pH that can be caused by two sources of acidity, H_2CO_3 and VFAs. The major requirement for a well-operating digester is the neutralization of the high carbonic acid concentration which results from the high partial pressure of carbon dioxide in the reactor. Sufficient alkalinity is essential for pH control. Alkalinity serves as a buffer that prevents rapid change in pH. The alkalinity is the result of the release of amino groups and production of ammonia as the proteinaeceous wastes are degraded.

pH and alkalinity in anaerobic digestion can be adjusted using several chemicals such as lime, sodium hydroxide or sodium bicarbonate. Chen et al., (2010) reported that alkalinity of about 2,500 mg $CaCO_3$/l and pH above 7 was maintained by adding 0.2 g NaOH/g VS. The results of this study indicated that it was necessary to use the chemicals, such as NaOH, to control the pH of the single-stage anaerobic digester treating the food waste. As the digestion proceeds and reaches the step of methanogenesis, protein degradation increases the ammonia concentration through release of amino groups. The produced ammonia acts as a buffer and during this time, pH can reach 8 or above. After stabilization of methanation, pH becomes stable between 7.2 and 8.2. Thus, in anaerobic digesters, ammonia is also responsible

for buffering, and stabilizes pH when present up to 1000 mg/l concentration (Fricke et al., 2007).

2.6.3 Volatile Fatty Acids Concentration

Volatile fatty acids (VFA) are important intermediate compounds in the metabolic pathway of methane fermentation and cause microbial stress if present in high concentrations. The intermediates produced during the anaerobic bio-degradation of an organic compound are mainly acetic acid, propionic acid, butyric acid, and valeric acid (Nayono, S. E., 2010). Among these, acetic and propionic acids are the major VFAs present during anaerobic bio-degradation and their concentrations provide a useful measure of digester performance. Acetate yield is increased slightly with increasing pH, whereas butyrate yield is increased with decreasing pH. Propionate yield was found to be unrelated to pH. The VFAs uptake might play a crucial role in the whole degradation kinetics of solid organic waste digestion, as the accumulation of the intermediate products, VFAs, is the rate-limiting step (Guendouz et al., 2010). High concentrations of VFAs in the digester would lower the pH, inhibit methanogenic activity and cause possible failure of the anaerobic digestion process. Vieitez et al., 2010) demonstrated that fermentative reactions stopped at a VFAs concentration of 13 g/l accompanied by a low pH of 5. The limiting step in anaerobic digestion is hydrolysis, which is usually inhibited by high propionate concentrations (Juanga 2005).

2.6.4 Temperature

Temperature is one of the major important parameters in anaerobic digestion as it determines the rate of anaerobic degradation processes

particularly the rates of hydrolysis and methanogenesis. Moreover, it not only influences the metabolic activities of the microbial population but also has a significant effect on some other factors such as gas transfer rates and settling characteristics of biosolids (Stronach et al., 1986 and Metcalf & Eddy Inc., 2003). There are two temperature ranges that provide optimum digestion conditions for the production of methane i.e. the mesophilic and thermophilic ranges. Most reactors operate at either mesophilic or thermophilic temperatures with optima at 35 and 55°C respectively (De La, 2006). Figure 2.2 graphically illustrates the direct relationship between the temperature and the rate of anaerobic digestion. For mesophilic range, temperature of 30-40°C needs to be maintained in the digester, whereas temperature range of 50-60°C is the range for thermophilic operation (Mata-Alvarez, 2002).

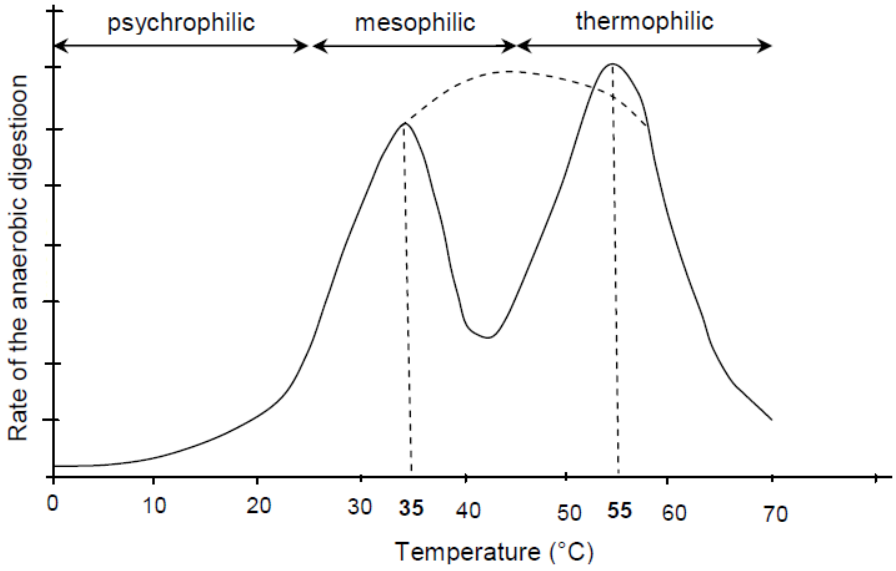


Figure 2.2 Graphical representation of temperature ranges for anaerobic digestion (*Source*: Mata-Alvarez et al., 2002)

Mesophilic bacteria are supposed to be more robust and can tolerate greater changes in the environmental parameters, including temperature. Although it requires longer retention time, the stability of the mesophilic process makes it more popular in current anaerobic digestion facilities (Zaher et al., 2009). A thermophilic temperature reduces the required retention time. The microbial growth, digestion capacity and biogas production could be enhanced by thermophilic digestion, since the specific growth rate of thermophilic microbes is higher than that of mesophilic microbes (Kim and Speece, 2002). Thermophilic anaerobic digestion has been reported to generate about 25-50% higher methane than mesophilic digestion (Khanal, 2008; Yilmaz et al., 2008). A study comparing the performance of thermophilic and mesophilic semi-dry digestion of mechanically sorted municipal solid waste (Cecchi et al., 1991) found that thermophilic process yielded gas production rate of 2-3 times more than the mesophilic process and better volatile solids elimination. However, thermophilic process is sometimes considered as less attractive from the energy point of view since it requires more energy for heating (Zaher et al., 2009). It should be noted that an increase in methane yield from the thermophilic process has to be balanced against the increased energy requirement for maintaining the reactor at the higher temperature (Amani et al., 2011). Thermophilic bacteria are very sensitive to small temperature-changes and so most of the digesters operate at mesophilic temperatures.

2.6.5 C/N ratio

The relationship between the amount of carbon and nitrogen present in organic materials is represented by the C/N ratio. A solid waste substrate with high C/N ratio is not suitable for bacterial growth due to deficiency of

nitrogen. As a result the gas production rate and solids degradability will be low. On the other hand, if the C/N ratio is very low, the degradation process leads to ammonia accumulation and hence pH value exceeding 8.5, which is toxic to the methanogenic bacteria (Hartmann and Ahring, 2006). Optimum C/N ratios in anaerobic digesters should be between 20–30 in order to ensure sufficient nitrogen supply for cell production and the degradation of the carbon present in the wastes (Fricke et al., 2007). Optimum C/N ratios of the digester materials can be achieved by mixing materials of high and low C/N ratios, such as organic solid waste mixed with sewage or animal manure (Verma, 2002).

2.6.6 Hydraulic Retention Time

The hydraulic retention time (HRT) is a measure to describe the average time that a certain substrate resides in a digester. The required retention time for completion of the anaerobic digestion reactions varies with technologies, process temperature, TS content and waste composition. The retention time for wastes treated in mesophilic digester is usually higher (up to 40 days) than that of thermophillic digesters which can be up to 8 days (Cecchi et al., 1991). Shortening the retention time decreases the reactor volume and hence saves capital cost. Increase in retention time, however, increases reactor stability. Hartmann and Ahring (2006) compiled the reports from other researchers and found that the HRT of anaerobic digesters treating solid wastes varied from 3 to 55 days, depending on the type of waste, operational temperature, process stage(s) and configuration of the digesters. The HRT for dry anaerobic digestion ranges between 14 and 30 days and for wet anaerobic processes it can be as low as 3 days (Zeshan, 2012). Thus, feedstock with high TS content needs long RT for digestion.

The HRT is the ratio of the digester volume to the influent substrate flow rate (eq. 2.9). Waste containing readily available biodegradable compounds such as sugar, require low HRT, whereas complex waste, e.g. lignin organic compounds, is slowly degradable and needs longer HRT for their decomposition.

$$HRT(d) = \frac{V}{Q} \quad \text{..... (2.9)}$$

Where, V = digester volume (m^3), Q = flow rate (m^3/d)

2.6.7 Organic Loading Rate

Organic loading rate (OLR) is a measure of the biological conversion capacity of the anaerobic digestion system.OLR is defined as the amount of organic matter (expressed as volatile solids or COD of the feeding substrate) that must be treated by a certain volume of anaerobic digester in a certain period of time. Mathematically OLR is expressed by equation (2.10). Volatile solids means (VS) how much mass of a dry sample that is oxidized when combusted at temperature 550°C.

$$OLR = \frac{QS}{V} \quad \text{.....(2.10)}$$

Where,

S = substrate concentration (kg substrate in terms of VS)

OLR = organic loading rate (kg substrate/ day x m^3digester)

Dry digesters can tolerate much higher OLR than the wet anaerobic digestion process. There is an optimum feed rate for a particular reactor which will produce maximum gas, and beyond which further increases in the quantity of substrate will not proportionately produce more gas

(Yadvika et al., 2004). Feeding the system above its sustainable OLR, results in low biogas yield due to accumulation of inhibiting substances such as fatty acids in the digester slurry. In such a case, the feeding rate to the system must be reduced. In continuous systems, OLR is an important control parameter. System failures have been reported by many plants due to overloading (RISE-AT, 1998).

Chaudhary (2008) has reported that the dry continuous anaerobic digestion reactor stabilizing source-sorted OFMSW showed stable performance with highest biogas yield (278.4 LCH4/kg VS) and VS reduction of around 59.21% during loading rate 2.5 kg VS/m^3/d in thermophilic condition among the three different OLRs of 2.5, 3.3 and 3.9 kg VS/m^3/d for constant retention time of 25 days.

2.7 Types of Anaerobic Digestion Systems

Typically anaerobic reactors or processes of solid waste can be distinguished into several types, mostly according to the feeding mode (continuous mode: single stage, two stages and batch mode) and the moisture content or total solid of the substrate (wet or dry digestion). Furthermore with those basic types, the anaerobic reactors can be arranged according to the digestion process temperature (mesophilic or thermophilic) and the shape of the reactors (vertical or horizontal).

A wide variety of systems have been developed to treat MSW anaerobically. They can be split into different categories as following:

- Dry versus wet digestion
- Continuous versus batch process

- Mesophilic versus thermopilic digestion
- Single stage versus multi-stage digestion

2.7.1 Dry and Wet Anaerobic Digestion

The dry anaerobic digestion process has been regarded as an innovative waste recycling approach to treat high-solid-content bio-wastes (>10%) in its produced form (De Baere, L., 2000; Schober et al., 1999). According to Tchobanoglous Low solids systems (LS) contain less than 10% TS, medium solids (MS) contain about 10%-15%, and high solids (HS) processes range from 20% to 40% (Tchobanoglous et al.,1993). However, there is no established standard for the cut-off point. With the dry digestion process, little or no water is added to the bio-waste. As a consequence, the material streams to be treated are minimized. The resulting advantages are smaller reactor volumes and easier dewatering of the digestate thus less costly reactors. Because of the low mobility in dry digestion, a defined residence time can be reached by approximating plug flow, which is particularly important for the sanitization of the solid product in the thermophilic operation process. The performance of dry digestion process is very robust as it allows very high production rates (Gunaseelan, V.N.,1997). This process also results in a lower production of leachate and easy handling of digested residues that can be further treated by aerobic composting processes or used as organic fertilizer (Brummeler et al., 1989b). The average methane content in biogas was about 66% in dry mesophilic anaerobic digestion of water sorted organic fraction of municipal solid waste (Li Dong et al., 2010; Liu G.T. et al., 2006). Though the dry anaerobic digestion process has attracted increased attention all around the world because of its reduced cost in digesters and slurry handling, the process

sometimes suffers from inhibition problems and is harder to control. First, the solid-state anaerobic digestion requires a larger amount of inoculum and much longer retention time. The retention time of dry digestion for farm wastes is approximately three times longer than wet digestion (Tchobanoglous et al., 1993). Second, the accumulation of volatile fatty acids (VFAs) restricts the biogas yield. Third, the medium (solid wastes) is complex and heterogeneous in the terms of structure, composition and size. The digester behaves as a viscoelastic material aggregate, ranging between 200 and 800 Pa (Garcia-Bernet et al., 2010). Thus, the complete mixing is hard to achieve. Therefore, this technology needs enhanced reliability of operation to become more sustainable (De Baere, 2006). The reactors used in dry anaerobic digestion processes generally do not apply mechanical mixers and may use biogas injection to perform mixing of the digester content (Luning et al., 2003). Dry anaerobic digestion offers less complicated pre-treatments and higher loading rate (10 kg VS/m^3/d or more).

In wet digestion processes, the solid waste has to be conditioned to the appropriate solids concentration by adding process water either by recirculation of the liquid effluent fraction, or by co digestion with a more liquid waste. The latter is an attractive method to combine several waste streams like sewage sludge or manure and OFMSW (Hartmann et al., 2006; Banks et al., 2007). Reactors used in wet digestion processes generally are referred to as continuous stirred tank reactors (CSTR), with application of mechanical mixers or a combination of mechanical mixing and biogas injection (Banks et al., 2007). The application of a wet digestion process offers several advantages such as dilution of inhibitory substances by process water and requirement of less sophisticated mechanical equipments.

However, disadvantages, such as complicated pre-treatment, high consumption of water and energy for heating and the reduction of working volume due to sedimentation of inert materials have to be taken into account (Chynoweth et al., 1994).

In general, both anaerobic digestion processes can be considered a proven technology for the treatment of organic solid waste. Luning et al., (2003) reported that biogas production figures of the wet digestion process (Waasa process) and the dry digestion process (Valorga process) were identical. The wet process produced more wastewater; however, this was compensated by a smaller amount of digestate to be disposed of and the separation of inert materials suitable for recycling.

Table 2.6 Advantages and disadvantages of high solids content

Advantages	Disadvantages
▪ Much smaller reactor volumes ▪ Less or no liquid effluent and less water consumption ▪ Smaller energy consumption for heating large volume ▪ Smaller dewatering equipment ▪ The plug flow ensure complete hygienization of the waste (at thermophilic temperatures)	▪ Slower anaerobic fermentation ▪ More robust, thus more expensive pumps and auxiliary equipment ▪ Less water available for diluting the salts present, thus salt concentration can reach toxic concentrations

2.7.2 Batch and Continuous Feeding Systems

Two feeding modes are generally used in anaerobic digestion of solid waste: the batch system and the continuous system. In a continuous process, the substrate is added to and removed from the digester continuously. Since

fresh substrate is added continuously, all reactions involved in biogas generation will occur at a fairly constant rate. This results in a fairly constant biogas production rate. Usually, two digesters are used in the continuous process and the substrates are digested in two stages. The advantage of this process is that the digesters can be used as storage devices.

In the batch process the substrate is fed into the digester and then the digester is sealed for the entire period without adding additional substrate until the decomposition process is near completion. Most of the digested substrate is then emptied and the digester is filled with new substrates, and then the digestion process starts again. In a batch process, the production of biogas is non-continuous. Gas production will peak at the middle of the process and will be low at the beginning and at the end of the process. Typically, in order to ensure a more steady supply of biogas, a number of batch digesters with substrates at different stages of anaerobic digestion are operated in parallel.

Table 2.7 Comparison of continuous and discontinuous feed

Process Operation	Continuous	Discontinuous
Retention time	Shorter	Longer
Technical equipment	Complex	Simple

2.7.3 Mesophilic and Thermophilic Digestion

Anaerobic digestion can take place at psychrophilic temperatures below 20°C, but most reactors operate at either mesophilic or thermophilic temperatures with optima at 35 and 55°C respectively, because the biomass activities and anaerobic treatment capacities have been significantly reduced

at lower temperature (Hartmann et al., 2006; Banks et al., 2007). The biodegradation of Hand Sorted Organic Fraction of MSW (HS-OFMSW) in CSTR type digesters at 35 ^{o}C resulted a maximum methane yield ranging from 0.39 to 0.43 m^3 /kg VS added without paper and wood and VS reduction ranged from 63 to 69 %. Furthermore, the methane yield of MS-OFMSW ranged from 0.11 to 0.16 m^3/kg VS added and VS reduction was found around 30 % due to its high ash value (Gunaseelan V.N, 1997; Bouallagui et al., 2004). However, the quantity of biogas produced as a function of the quantity of introduced raw material will be variable according to several factors such as the quality of the organic matter and the environmental parameters.

In the thermophilic high solids anaerobic digestion, higher OLR and methane production rate can be achieved at reduced HRT. Gunaseelan (1997) studied that the methane yield was around 0.2 m^3 /kg VS added. Digestion under thermophilic condition has many advantages such as higher metabolic rates and a high destruction of pathogens and weed seeds. On the other hand, thermophilic treatment has some drawbacks such as less stability compared to mesophilic conditions. Furthermore, the energy requirements of thermophilic systems are higher than those of mesophilic systems. The effect of temperature is particularly important on the hydrolysis step. The hydrolysis rate of cellulose in thermophilic conditions is about 5 - 6 times higher than that observed in mesophilic conditions (Bouallagui et al., 2004). The advantages and disadvantages of operating the anaerobic digestion process in mesophilic and thermophilic ranges are described in Table 2.8.

Table 2.8 Comparison between mesophilic and thermophilic anaerobic digestion

Parameter	Mesophilic	Thermophilic
Temperature	30 - 40 ^{0} C	50 - 60 ^{0} C
Residence time	15 - 30 days	10 - 20 days
Total solids (wet) (dry)	 10 -15 % 20 - 40%	 10 – 15 % 20 – 40%
Advantages	▪ More robust and tolerant process than thermophilic	▪ Higher gas production ▪ Faster throughput ▪ Process more sensitive to environmental variables
Disadvantages	▪ Lower gas production rate, hence larger digestion tanks ▪ Separate sanitization stage	▪ Needs effective control ▪ Separate sanitization stage

2.7.4 Single Stage versus Multi Stage Digestion

Anaerobic fermentation of bio-waste can be operated by one-stage or two-stage fermentation. In the one-stage process all fermentation stages (e.g. hydrolysis, acidification, acidification and methanogenesis) take place in one reactor; therefore, optimum reaction conditions for the overall process are not achieved, due to the different environmental requirements during the various stages of the fermentation. Therefore, the degradation rate is reduced and consequently the retention time increases. The basic advantage of one stage process operation is the relatively simple technical installation and operation of the anaerobic digestion plant, whereas the costs are lower. The major drawback of single stage digester systems is that these processes are required to proceed under the same operating conditions despite

differences in growth rates and optimal pH of the microbial groups involved in each step. This is the reason why single stage systems are more easily to upset compared to multi stage systems. This disadvantage is substantial especially in the case of substrates where degradation is limited by methanogenesis rather than by hydrolysis, e.g. cellulose poor kitchen wastes. These wastes, being very rapidly acidified, tend to inhibit the methanogenesis when the feedstock is not adequately mixed, buffered and dosed (Geradi et al., 2003; Vandevievere et al.,2002; Veekan et al., 2000).

In two-stage processes the hydrolysis and acidification take place in one bioreactor, while methanogenesis is carried out in a separate reactors thus providing flexibility to optimise each of these reactions so that mixing and adjustment of the pH can be optimized separately, permitting higher degradation degrees and loading rates. In two-stage processes the retention time of the substrate is significantly decreased. However, such systems involve more sophisticated technical design and operation and subsequently higher costs. In the first reactor, organic fraction is hydrolysed producing dissolved organics, organic acids, CO_2 and low concentrations of hydrogen. The reaction rate in the first reactor is limited by the rate of hydrolysis of cellulose. In the second stage the highly concentrated water is supplied to an anaerobic fixed-film reactor, sludge blanket reactor, or other appropriate system where methane and CO_2 are produced as final products. In the second reactor the rate of reaction is limited by microbial growth. The potential drawback of two/multi stages systems is the decrease of biogas yield due to solid particles removal from the feedstock to the second stage (Vandevivere et al, 1999).

2.8 Commercial Anaerobic Digesters for Treating Organic Solid Waste

Stimulated by the increasing demand of anaerobic digester for organic solid wastes, several commercial anaerobic digester plant designs have been developed over the past two decades. Especially in European countries, there are many different processes available on the market. The processes are patented according to several basic characteristics as previously discussed (batch or continuous feeding, number of stages, total solids content of waste and operating temperature). Mixing methods (gas injection or mechanical stirrers), reactor type (vertical or horizontal, rectangular or cylindrical) and process flow (completely mixed or plug flow) are also parameters to obtain patent rights. Several patented processes have been successfully proven their reliable performance in full scale plants. More detailed concepts of processes namely BIOCEL (batch system), DRANCO, Valorga, KOMPOGAS (one stage dry system), Waasa, BTA (one stage wet system). Figure 2.3 shows the simplified diagram of different designs of single stage dry anaerobic digester.

BIOCEL: The system is based on a batch-wise dry anaerobic digestion. The total solids concentration of organic solid wastes as feeding substrate is maintained at 30–40% dry matter (w/w). The process is accomplished in several rectangular concrete digesters at mesophilic temperature. The floors of the digesters are perforated and equipped with a chamber below for leachate collection. Prior to feeding, fresh bio-waste substrate and inocula (digestate from previous feeding) are mixed then loaded to the digester by shovels. After the loading is finished, the digesters are closed with air tight doors. In order to

control the odour emission; the system is housed in a closed building that is kept at a slight under-pressure. The temperature is controlled at 35–40ºC by spraying leachate, which is pre-heated by a heat exchanger, from nozzles on top of the digesters. Typical retention time in this process is reported to be 15-21 days (Ten Brummeler, 2000).

In the DRANCO process, feed is introduced daily into the top of the reactor by pumping through the feed tubes, and the digested waste is removed from the bottom at the same time. Part of the digested waste is used as inoculums (one part of fresh waste for six parts of digested waste) while the rest is dewatered to obtain an organic compost material. There are no mixing devices in the reactor other than the natural downward movement of the waste. This process focuses on the conversion of the organic fraction of the municipal solid wastes to energy and a humus-like final product, called Humotex. The operating temperature is 55 ^{o}C, the total solids concentration is 32% and the residence time is around 18 days (Vandevivere et al., 2002; De Baere, 2006).

VALORGA: The Valorga system is quite different in that the horizontal plug-flow is circular in a vertical cylindrical reactor, which is partially partitioned (around 2/3rd of the reactor) by a central wall or baffle. The partition wall is connected to reactor wall at one end, while the other end is free allowing the passage of waste. The inlet is on one side of the baffle while outlet is on the other side. The waste is forced to move around the baffle from inlet to outlet that creates a plug-flow. Moreover, mixing is done by biogas injection at a high pressure at the bottom of the reactor. This biogas injection takes place every 15 minutes through a network of injectors. The residence time is between 18-25 days at 37^{o}C and solids

content is kept at 30%. The Valorga process is ill suited for relatively wet wastes because sedimentation of heavy particles inside the reactor takes place when the total solids content is less than 20% (Lissens et al., 2001). Possible drawbacks of this system are the clogging of the gas injection ports and the overall maintenance.

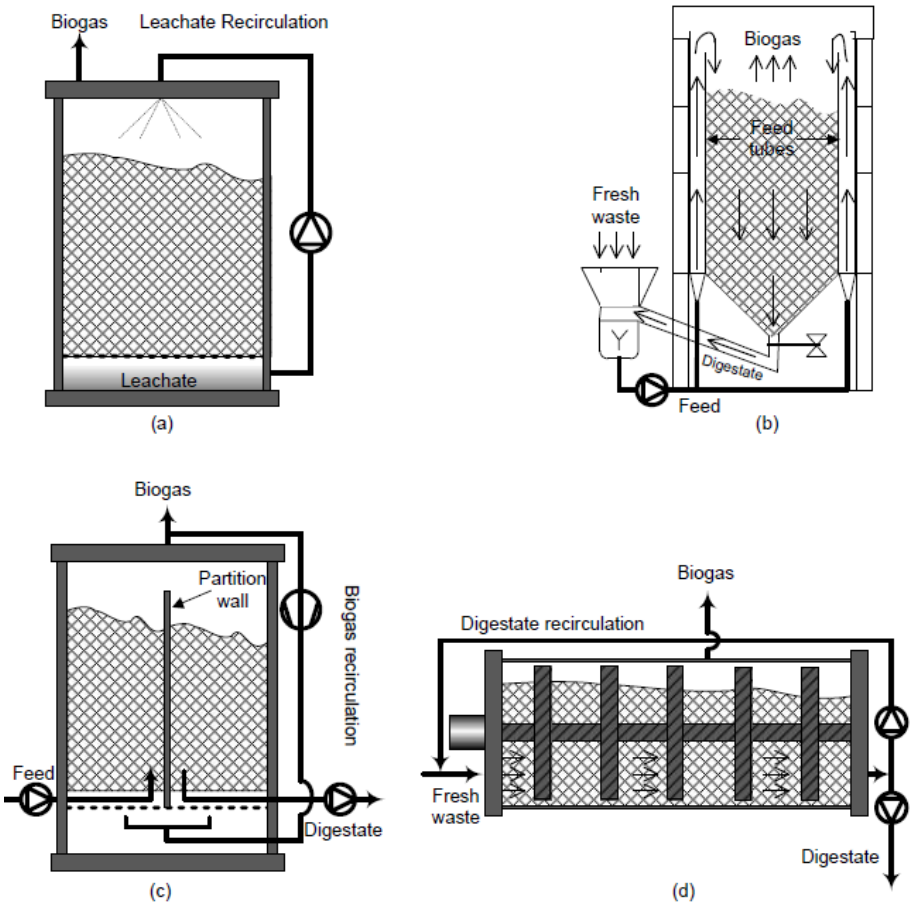


Figure 2.3 Designs of single-stage dry anaerobic digesters, (a) BIOCEL, (b) DRANCO, (c) VALORGA, (d) KOMPOGAS

The KOMPOGAS process works similarly, except that the plug flow takes place horizontally in cylindrical reactors. The digested material is

removed from the far end of the reactor after approximately 20 days. The horizontal plug flow is aided by slowly rotating impellers inside the reactors, which also serve for homogenization, degassing, and resuspending heavier particles. This process runs at 55^{o}C and requires careful adjustment of the solid content around 23% TS inside the reactor. At lower values, heavy particles such as sand and glass tend to sink and accumulate inside the reactor while higher TS values cause excessive resistance to the flow. The most significant factor of tubular reactor is its ability to separate acidogenesis and methanogenesis longitudinally down the reactor, allowing the reactor to behave as a system of two phases (Bouallagui et al., 2005).

In India, in the recent decade, as a result of Ministry of Non-Conventional Energy Sources (MNES) programs, there has been much interest in generating power through biomethanation of municipal solid waste. Various institutions and NGO's have been involved in the development of technologies. The development was more focused on low-tech digesters applicable for local conditions in India. Following types of low-tech anaerobic digesters are implemented in India, at least on a pilot scale level (Christian Muller et al., 2007).

- TEAM digester (developed by The Energy and Resource Institute (TERI), New Delhi)
- ASTRA digester (Centre for Sustainable Technologies, Bangalore): this type of biogas plants are built by TIDE (Technology Informatics Design Endeavour)
- ARTI digester (Appropriate Rural Technology Institute,Pune)
- SPRERI digester (Sardar Patel Renewable Energy Research Institute)

- BARC digester (Bhabha Atomic Research Institute, Mumbai)
- BIOTECH, Thiruvananthapuram.

2.9 Process Improvement for Anaerobic Digestion

Many researches and reports have been conducted regarding almost every aspect of anaerobic digestion of solid waste which is useful for process improvement or to actualize a more robust reactor design. Some authors focused on the kinetics of anaerobic biodegradation of complex waste such as OFMSW which is considered as a key issue for the understanding of the process and for the design of treatment units. Mata Alvarez, for instance, compiled the first order kinetic constant values for hydrolysis (which is considered as rate limiting step in anaerobic digestion of solid waste) of different materials (Mata Alvarez et al., 2000). Other papers reported the performance of different reactor configurations (one stage or multi stage, dry or wet) and effects of inhibition substances, as well as effects of basic parameters such as pH, temperature, mixing.

Co digestion of OFMSW with other types of waste is an interesting alternative to improve biogas production, to obtain a more stable process and to achieve a better handling of waste. However, some possible disadvantages (e.g. transport costs of co substrate, additional pre-treatment facilities and the problems arising from the harmonization of the waste generators) have to be taken into account. The key factor of successful co digestion is that the balance of macro and micro nutrients can be assured by co substrate.

Various types of solid waste streams such as sewage sludge, animal manure and organic industrial waste have been proposed as co substrate for

anaerobic digestion of OFMSW. However, there are recent studies claimed that the addition of wastewater treatment plant sludge's and dairy manure help to elevate the gas production rate and increase the reactor stability (Winter et al., 2009 and Nayono, 2010). A recent study conducted by Lopez et al affirms that the addition of inoculums (sludge and animal manure) could increase the microbial population and definitely could improve the performance of the process (Lopez et al., 2008). Thus, co-digestion is an interesting part of the process to be investigated on various substrates.

2.10 Summary and Needs for the Present Study

This chapter has presented a detailed survey of literature in the area of anaerobic digestion. Intensive research during the past twenty years has proved that AD technology is a viable option for the treatment of OFMSW. Various factors affecting the anaerobic digestion of bio-waste were discussed. A wide variety of systems, which have been developed to treat OFMSW were also discussed.

The dry anaerobic digestion (DAD) process has been regarded as an innovative waste recycling approach to treat high solid content bio-wastes (>15%) in its produced form. Various research studies on dry anaerobic digestion have been conducted at TS content of 15-30% using different substrates (Table 2.9). DAD technology has tremendous application in the future for sustainability of both environment and agriculture because it represents a feasible and effective waste-stabilization method to convert the undiluted solid bio-waste into renewable energy with nutrient rich organic fertilizer.

Table 2.9 Operational characteristics of dry anaerobic digesters

Substrate	Feed (TS %)	Reactor type	Tempe-rature (°C)	RT (day)	OLR(kgVS/ m^3/day)	Optimal gas yield (LCH_4/kg VS)	Configuration	VS reduction (%)	Reference
Cow manure +Sludge	15-16	Batch	30	60	-	314	Single phase	41.8	Li et al., 2010
SS-OFMSW	20	Batch	55	60	-	290	Single phase	45	Forster-carneiro, 2008b
OFMSW	20	Continuous, plug flow	55	25	2.5	278.4	Single phase	59.21	Chaudhary,2008
Municipal solid waste	12-16	Batch	55	28	-	320	Single phase	86	Juanga, 2005
Municipal solid waste	35	Batch with paddle mixer	35	30-40	-	200	Single phase	-	Guendouz et al., (2010)
Food wastes	20	Batch	37	120	-	373	two phase	90	Cho et al, 1995
MS-OFMSW	25-30	Continuo-us CSTR	55	25-40	4.42-7.5	300	Single phase	80	Montero et al., (2008)
Sewage sludge	20	Continuo-us CSTR	35	12	8.5	190	Single phase	29	Duan et al., (2012)
SS-OFMSW	20	Continuous CSTR	55	11	12.1	490	Single phase	59.3	Pavan et al., (2000
SS-OFMSW	20	Continuous CSTR	55	15	9.2	230	Single phase	-	Bolzonella et al.,(2003)
FW + Paper waste	30	Contnuous with lateral impeller	35	30-100	10	250	Single phase	80	Kim and Oh, (2011)
OFMSW	12	Batch	35	65-70	-	360	Single phase	65	Li Dong et al.,(2010)

However, there is limited practice for the application of this process especially in developing countries due to the lack of appropriate treatment system configurations and longer time required for the bio stabilization of waste. To reduce the retention time, semi-dry digestion (TS is between 10% and 15%) can be practiced. Therefore the purpose of the present study is to develop feasible semi-dry anaerobic digestion process for the treatment of OFMSW for potential energy recovery and sustainable waste management.

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Chapter 3

MATERIALS AND METHODS

Contents

3.1 Introduction

This chapter explains the research methodology that was used in order to acquire the objectives mentioned in chapter 1. This chapter gives an outline of major experiments done in three phases; Phase I, II and III. In Phase I, batch study of OFMSW at mesophilic temperature at different substrate concentration was conducted. Phase II consists of batch study of OFMSW at thermophilic temperature. Phase III gives bench scale study of continuous digestion system focused on optimization of semi- dry anaerobic digestion in terms of organic loading rates.

3.2 Organic Fraction of Municipal Solid Waste as Feed Stock

Organic fraction of MSW was taken as the substrate for this experiment. The waste was collected from nearby vegetable market and households at

Thrissur, Kerala, India. The composition of feed stock is shown in Table 3.1. The wastes were sorted and shredded, then mixed several times in laboratory and kept at 4°C until used.

Table 3.1 Composition of substrate

Feed stock type	Percentage (%)
Vegetable wast	35
Fruit waste	25
Food waste	37
Paper	3

3.3 Inoculum

Inoculum source is a very important operational parameter. The percentage of inoculation for acidogenic fermentation of organic urban wastes is approximately 30% (w/w) (Carreiro et al., 2006). The inoculum used in this study was fresh cattle dung which contains all the required microbes essential for anaerobic digestion process. The inoculum was collected from nearby farm and kept at 4°C until used. The pH, total solid and volatile solid of the inoculum were 6.5, 25.2% and 85.9% respectively.

3.4 Phase I: Batch Study for AD of OFMSW at Mesophilic Temperature

3.4.1 Experimental Set up

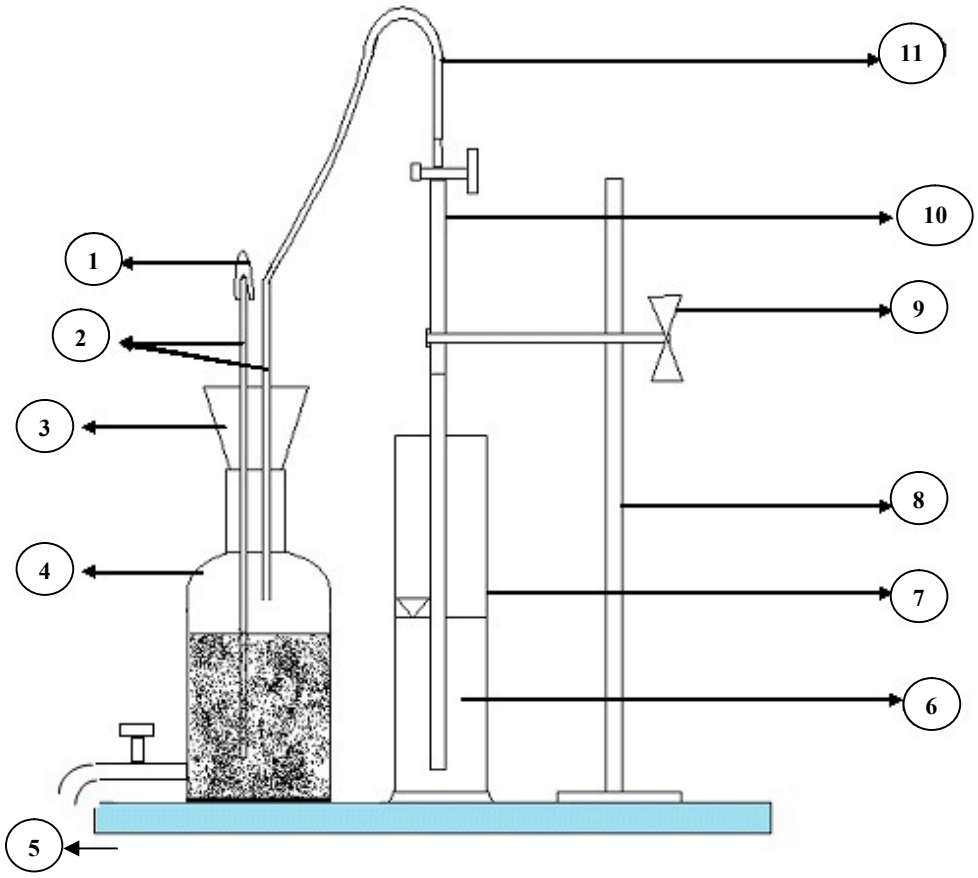
The experiments were carried on batch laboratory scale reactor (aspirator bottle) with total capacity of 2 L. The reactor was made of borosilicate glass with bottom sampling outlet. The bottles were closed by rubber stoppers equipped with glass tubes for gas removal and for adjusting the pH. The glass tube was dipped inside the slurry to avoid gas loss during

the pH adjustments. The effective volume of the reactor was maintained at 1.6 L. Biogas production from the reactors was monitored daily by water displacement method. The volume of water displaced from the burette was equivalent to the volume of gas generated. The reactor was mixed manually by means of shaking and swirling once in a day. The reactors were operated at room temperature (32 ºC). The schematic diagram of the experimental set up is shown in Figure 3.1. Photograph of the experimental system is shown in Figure 3.2.

3.4.2 Experimental Procedure

The study is programmed to evaluate the mesophilic digestion of OFMSW at three different initial substrate concentrations. The substrate concentration was expressed as weight of solids/total volume of solids plus water, assuming that the density of the solids is approximately equal to the density of water. Three reactors were used of 2 L total volume and 1.6 L effective volume at discontinuous condition but different total solids concentrations of 115 g/l, 99 g/l and 83 g/l respectively. All the reactors were fed with municipal garbage, tap water and cattle dung slurry (inoculum), used as the starter in the reactors. Liquid samples were drawn from each reactor periodically and analysed for pH, volatile fatty acids, alkalinity chemical oxygen demand and ammonia nitrogen. The pH was measured every 2 days and it was maintained in the range of 6.5 to 7.5 using 6N sodium hydroxide solution as which is the optimum range for methanogens growth (Pavan et al., 2000). Volatile fatty acids, alkalinity chemical oxygen demand and ammonia nitrogen were analysed once in a week. Daily biogas production was measured by water displacement method. The substrate was mixed once each day, at the time of the gas

measurement, to maintain intimate contact between the microorganisms and the substrate.



1. Sealing Clip
2. Glass tubes
3. Rubber stopper
4. Anaerobic digester
5. Outlet pipe
6. Saturated NaCl solution
7. Graduated cylinder
8. Stand
9. Clamp
10. Graduated burette
11. Rubber hose

Figure 3.1 Schematic diagram of the experimental set up

Figure 3.2 Experimental setup of batch study

3.4.3 Kinetic Study

Kinetic studies of anaerobic digestion process are useful to predict the performance of digesters and design appropriate digesters. Kinetic studies are also helpful in understanding inhibitory mechanisms of biodegradation. First-order kinetic models are the simplest models applied to the anaerobic digestion of complex substrates as they provide a simple basis for comparing stable process performance under practical conditions. Therefore, a first order model based on the availability of substrate as the limiting factor was used (M. S. Rao and S. P. Singh, 2004; Sanchez et al., 1996) to perform the present study. The basic equation is

$$\frac{dB}{dt} = -kB \quad \text{.....(3.1)}$$

where, k is the first-order substrate utilisation rate constant (time-1) and B (mg/l) represents the biodegradable substrate concentration.

On integration, Eq. (3.1) becomes

$$B=B_0 \exp(-kt) \quad \text{.....(3.2)}$$

where, B_0 (mg/l) represents initial substrate concentration.

Substrate concentration can be correlated with biogas production (G), as mentioned below.

$$\frac{G_\infty - G}{G_\infty} = \frac{B}{B_0} \quad \text{.....(3.3)}$$

where, G_∞ is the ultimate biogas production.

From equations (3.2) and (3.3), the integrated equation for the first order model which gives an analytical relation between the volume of biogas produced and digestion time was obtained and used to quantify the extent of process inhibition is as follows:

$$G = G_\infty[1 - e^{-kt}] \quad \text{.....(3.4)}$$

where k ($time^{-1}$) is the first-order biogas production rate.

Taking Napierian logarithms in the above equation and ordering the terms the following equation is obtained.

$$ln\left(\frac{G_\infty}{G_\infty - G}\right) = kt \quad \text{.....(3.5)}$$

Equation (3.5) indicate that $ln\left(\frac{G_\infty}{G_\infty - G}\right)$ versus t should give a straight line of slope equal to k with intercept zero. The value of G_∞ has been considered equal to the volume of biogas accumulated at the end of each experiment. Representation of the experimental data in the above equation gives straight line with intercept practically zero and slope equal to k. The values G_∞ and k were obtained from a non-linear regression analysis using Curve Expert 1.4.

3.4.4 Theoretical Optimization- Statistical Analysis

Design of experiment (DOE) is a well-accepted statistical technique able to design and optimize the experimental process that involves choosing the optimal experimental design and estimate the effect of the several variables independently and also the interactions simultaneously. Response surface methodology (RSM) is a statistical method used for experimental modelling and analysing the relationship between the input and response variables (Montgomery, 2005; Chong et.al., 2009; Bezerra et.al., 2008). In this study three process variables viz. initial pH, substrate concentration and TOC were selected to study the effect on biogas production. Analysis of variance (ANOVA) was used for analysis of regression coefficient, prediction equations, and case statistics. The experimental results of RSM were fitted using the following second order polynomial equation:

$$Y = \beta o + \Sigma \beta i Xi + \Sigma \beta ii Xi2 + \Sigma \beta ij Xi Xj \quad (3.6)$$

In this polynomial equation, Y is the predicted, Xi, Xj are independent variables, βo is the intercept term, βi is the linear coefficient, βii is the quadratic coefficient, and βij is the interaction coefficient.

In this study, the independent variables were coded as A, B and C. Thus, the second order polynomial equation can be represented as

$$Y = \beta o + \beta 1A + \beta 2A + \beta 3A + \beta 11A2 + \beta 22B2 + \beta 33C2 + \beta 12AB + \beta 23BC + \beta 13AC \quad \text{.....(3.7)}$$

Diagnostics Plots and model graphs were obtained using the Stat-Ease software with Design Expert v.8 to analyse the effects of variables individually and their interactions to determine their optimum level. The point prediction method was used for optimization of the levels of each variable for maximum response. 3-D surfaces and 2-D contour plots were developed using the quadratic polynomial equation obtained from regression analysis of experimental data by keeping two of the independent variables at a constant value while changing the other two variables.

3.5 Phase II: Batch Study for AD of OFMSW at Thermophilic Temperature

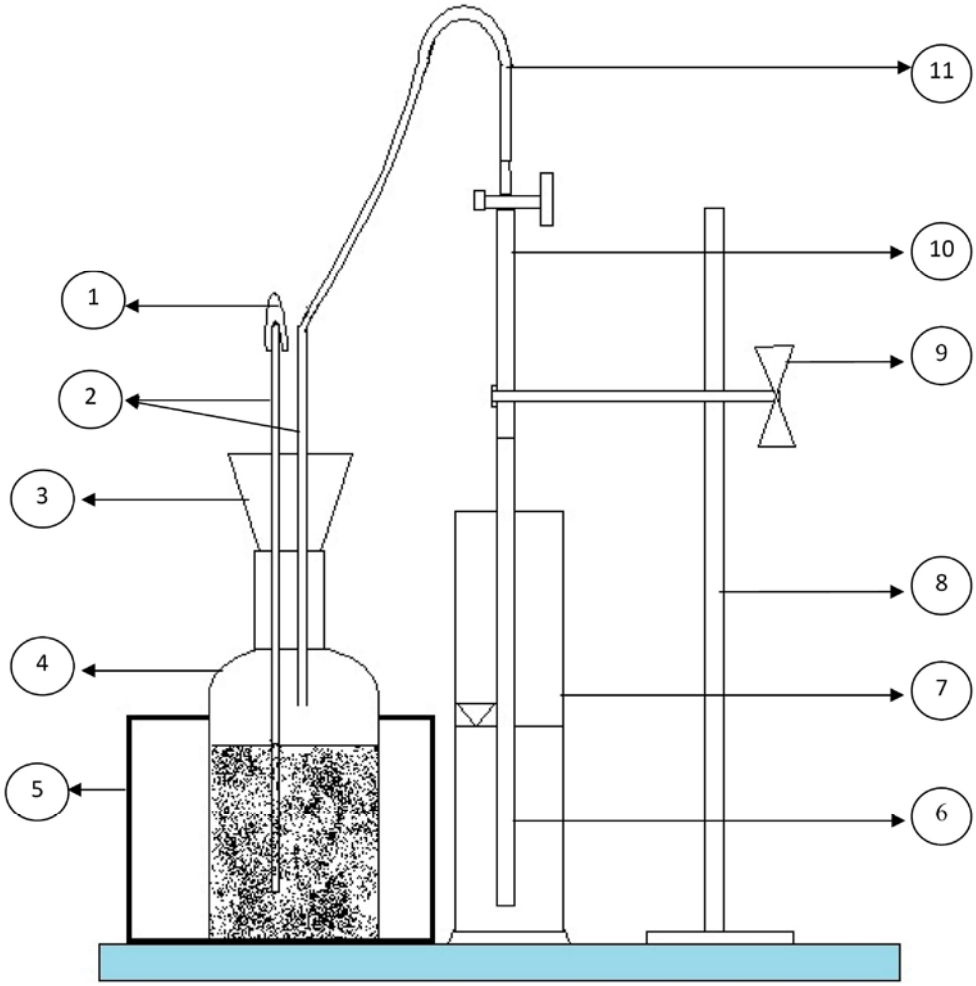
3.5.1 Experimental Set up

The experiment was carried on batch laboratory scale reactor with total capacity of 1 L. The reactor was made of borosilicate glass. The bottles were closed by rubber stoppers equipped with glass tubes for gas removal and for adjusting the pH. Schematic diagram of the experimental set up is shown in the Figure 3.3. The glass tube was dipped inside the slurry to avoid gas loss during the pH adjustments. The effective volume of the reactor was maintained at 800 ml. Biogas production from the reactors was monitored daily by water displacement method. The volume of water displaced from the bottle was equivalent to the volume of gas generated. The reactor was mixed manually by means of shaking and

swirling once in a day and it was operated at thermophilic condition (50°C) using a constant temperature water bath. The photograph of the experimental system is shown in Figure 3.4.

3.5.2 Experimental Procedure

The study is programmed to evaluate the thermophilic digestion of OFMSW at the substrate concentrations of 100 g/l. As per the previous study of the author (Sajeena et al., 2014), the optimum substrate concentration obtained was 100 g/l. The substrate concentration was expressed as weight of solids/total volume of solids plus water, assuming that the density of the solids is approximately equal to the density of water. The substrate was mixed well with inoculums before loading to the reactor to initiate the digestion process. Separate inoculum acclimatization was not conducted. However, the reactor's temperature was started in mesophilic (34°C) and then the temperature was gradually increased by 2°C/day until the optimum thermophilic (50°C) was reached (Chea Eliyan et al., 2007). This is used as a strategy to avoid the temperature shock load to microorganisms.



1. Sealing Clip
2. Glass tubes
3. Rubber stopper
4. Anaerobic digester
5. Constant temperature water bath
6. Saturated NaCl solution
7. Graduated cylinder
8. Stand
9. Clamp
10. Graduated burette
11. Rubber hose

Figure 3.3 Schematic diagram of experimental set up at thermophilic temperature

Figure 3.4 Experimental setup of batch study at thermophilic temperature

The reactor was fed with municipal garbage, tap water and cattle dung slurry (inoculum), used as the starter in the reactor. Liquid sample was drawn from each reactor periodically and analysed for pH, volatile fatty acids (VFA), alkalinity, chemical oxygen demand (COD) and ammonia nitrogen (NH_3-N). The pH was measured every 2 days and it was maintained in the range of 6.5 to 7.5 using 6N sodium hydroxide solution as which is the optimum range for methanogens growth (Banks, C.J et al.,

2008). Volatile fatty acids, alkalinity, chemical oxygen demand and ammonia nitrogen were analysed every 5 days. Daily biogas production was measured by water displacement method. The substrate was mixed once each day, at the time of the gas measurement, to maintain intimate contact between the microorganisms and the substrate. The experiment was carried out for 45 days at thermophilic condition (50°C) and at the end of the digestion the residue is collected, weighed and analysed for total solid (TS),volatile solid (VS) and ash content. The amount of leachate was also measured and analysed for pH, VFA, COD, NH_3-N, total organic carbon (TOC) and alkalinity.

3.6 Phase III: Bench Scale Study for Continuous Digestion System

3.6.1 Experimental Set-up for Bench Scale Study

A semi continuous bench scale study was carried out to achieve the objectives mentioned in chapter 1. A single stage anaerobic digester was operated at different organic loading rates to optimize the biogas production and to investigate operational parameters. The digester was designed according to the organic loading rate and the hydraulic retention time. The schematic diagram of the experimental setup is shown in the Figure 3.5. The digester, made up of transparent acrylic sheet, was designed for a total volume of 36.8 L and working volume of 29.4 L (80% of total volume). The lower portion of the reactor was of conical shape making the collection of drain leachate easy. A perforated plate of hole size 2 mm was fitted inside with conical bottom. A bottom pipe was connected to collect the leachate produced and the pipe was connected with peristaltic pump (Ener Tech) which was used for recirculation purpose. To obtain a homogeneous

suspension, liquid from the bottom of the reactor was withdrawn by a peristaltic pump and recirculate through the top of the reactor.

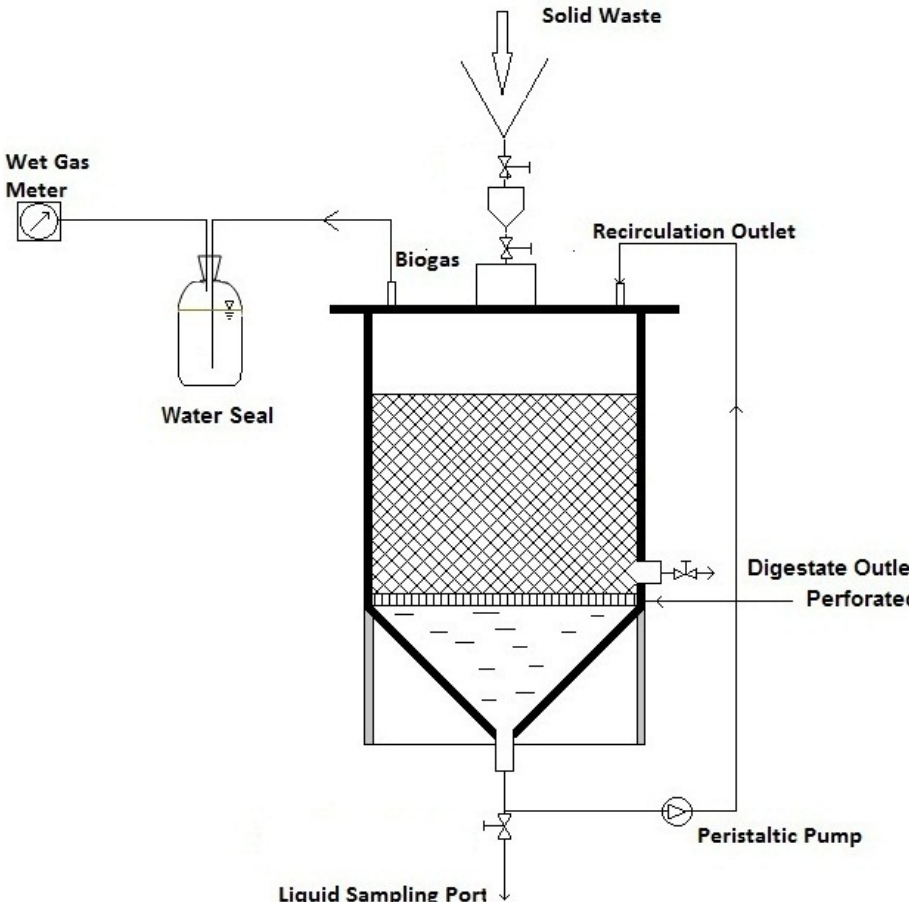


Figure 3.5 Schematic diagram of experimental setup for continuous study

Furthermore, the reactor was externally connected with the waste feeding hopper, wet gas meter (INSCIN) to measure the biogas flow, water seal and digested residue collection opening for continuous operation. As per the required waste load, daily feeding was done from the top while almost the same quantity of the digestate was removed from the reactor. The system was operated in semi- continuous mode with daily feeding one time

per day. The photograph of the experimental system for continuous study is shown in Figure 3.6.

Figure 3.6 Experimental setup of semi-dry anaerobic digester for continuous study

3.6.2 Experimental Conditions for Bench Scale Study

In this experiment, optimization of semi dry anaerobic digestion at room temperature (mesophilic, 32^{o}C) by testing the effect of different OLRs was studied. The study included start-up operation and continuous operation. The details of experimental conditions are given in the following subsections.

a) Start-up operation

Fresh organic fractions of MSW and inoculum were used as feed to the bioreactor. Organic fraction of MSW consists of food waste, fruit waste, vegetable waste from nearby vegetable market and house hold. Composition of substrate is given in Table 3.1. The wastes were sorted and shredded, then mixed several times in laboratory and kept at 4°C until used. The inoculum used in this study was fresh cattle dung which contains all the required microbes essential for anaerobic digestion process. The inoculum was collected from nearby farm and kept at 4°C until used. The pH, total solid and volatile solid of the inoculum were 6.5, 26.2% and 82.5% respectively. For the start-up operation, the prepared feedstock was loaded into the reactor after mixing well with the inoculums. The reactor was initially loaded with 12 kg of feedstock and 3.6 kg of inoculum source. Water was added to obtain the desired total solid concentration. The substrate concentration is expressed in terms of total solid. The TS concentration of the feed was 12%. It was a semi-dry digestion system. The system was operated without loading any additional feedstock, for first 50 days and it is considered as start-up phase. During the initial start-up phase, the system pH was neutralized using commercial caustic soda (6N NaOH) for quick onset of methanogenesis in the digester. The amount of NaOH required for the pH adjustment was calculated based on the simple laboratory tests using 100 ml of digestate from the digester and pH meter. To obtain a homogeneous suspension, leachate from the bottom of the reactor was recirculating by a peristaltic pump (Ener Tech) at the rate of 0.08 L/min for 6 hours daily. During these periods, the system was continuously monitored for the fluctuations in process parameters such as biogas, ammonia-N, COD,

TOC, volatile fatty acids (VFA), alkalinity and pH. The pH of digestate was analysed every 2 days, whereas all other parameters were analysed once in a week to interpret the process performance.

b) Continuous operation

The reactor was operated in a continuous mode from day 51 onwards by loading the reactor with designed OLRs. As detailed in Table 3.2, the feedstock was loaded into the reactor with different OLRs of 3.1, 4.2 and 5.65 kg VS/m^3/d in three consecutive runs (1 to 3) with constant retention time of 30 days. Each run continued until the biogas yield attained to its steady state, with no further increment, in the digester. To obtain a homogeneous suspension, leachate from the bottom of the reactor was recirculating by a peristaltic pump (Ener Tech) at the rate of 0.08 L/min for 6 hrs daily. Every time for feeding, one part of the fresh feedstock was mixed up with the two parts (wt./wt. basis) of digestate collected from the reactor. As per the required waste load, daily feeding was done from the top while almost the same quantity of the digestate was removed from the bottom of the reactor. Feeding and digestate withdrawal was done once a day. During these periods, the system was continuously monitored for the fluctuations in process parameters such as biogas, ammonia-N, COD, volatile fatty acids , alkalinity and pH as well as other digestate parameters (TS, VS, and TOC). The pH was measured every 2 days, whereas all other parameters were analysed once to twice a week to interpret the process performance.

Table 3.2 Operating conditions of bench scale experimental reactor

Run	Loading rate (kg/day)	OLR (kg VS/m^3 /d)	Retention Time (day)
Start up	-	-	50
Continuous 1	0.85	3.1	30
2	1.3	4.2	30
3	1.5	5.65	30

The digestate after being withdrawn from the anaerobic digester was dewatered using a strainer to separate liquid fraction (leachate) and solid fraction. Digestate from anaerobic digestion of municipal solid waste is an important issue due to wide variation in its characteristics. The digestate characteristics depend on origin of feedstock, type of feedstock and type of digestion process. Literature shows the digestate has certain amount of plant nutrients and organic matter and can be used as organic fertilizer or soil conditioner.

3.7 Analytical Methods

The analysis in this study was made for feedstock, inoculum sources and digested residues (as solid samples) for their physico-chemical characteristics such as total solid, volatile solid, carbon (as TOC) and nitrogen (as TKN). These parameters were used to compare the system performances and were controlled to provide the stability of the system. Liquid portion of the digested residues (leachate) was used for analysis of pH, alkalinity, VFA, TOC and ammonia nitrogen. All analytical determinations were performed according to "Standard Methods" (APHA, 1998).

3.7.1 Solid Waste Analysis

Solid waste analysis was conducted before feeding into the digester and after withdrawing the digestate from digester.

a) Moisture content determination

The percentage moisture of the MSW samples was determined by weighing about 50-100 g of the samples into a pre-weighed dish and drying the samples in an oven at 105 ^{o}C for 24 hours to a constant weight. The percentage moisture content (MC) and total solids (TS) were calculated using equations (3.8) and (3.9). The analysis was conducted in duplicates. After determining the moisture content, the samples were further tested for volatile matter content as explained in the section that follows.

$$\% MC = [(Wet\ Weight - Dry\ Weight)/ Wet\ Weight] \times 100 \quad \text{..... (3.8)}$$

$$\% TS = 100 - \% MC \quad \text{..... (3.9)}$$

b) Volatile solid determination

The volatile solid (VS) content was determined by the method of ignition of the sample at 550 °C for 1 hour. The same sample as was determined for moisture content and total solid was used for determining volatile solids. The dried samples were pulverized into fine solids and were mixed properly to ensure homogeneity. After that the pulverized samples were weighed for 2 grams and were placed on several evaporating dishes. Then the sample was evaporated for at least 1 hour at 550 ^{o}C in the muffle furnace. After drying the sample was placed into desiccators for cooling and was weighed immediately by using analytical balance. Thus volatile solid was calculated using eq. (3.10).

$$\% \text{ VS} = (w_0 - w_f / w_0 - w_e) \times 100 \quad \text{.....(3.10)}$$

Where,

w_0 = weight of sample and evaporating dish after 105^oC

w_f = weight of sample and evaporating dish after 550^oC

w_e = weight of empty dish

c) Total solids and Volatile solids loss determination

The mass balance of the digester is presented on Figure 3.7. The feedstock entering into the digester for AD process has an initial total wet weight of TW_0 and dry mater M_0. The residue for the overall process has the final total weight of TW_1 and dry matter M_1.Total solid loss can be determined by using eq. (3.11). The eq. (3.12) gives the dry weight of material before feeding into the digester whereas eq. (3.13) depicts the dry weight of digestate. For calculating the loss of volatile solid, eq. (3.14) can be used. Similarly equations (3.15) and (3.16) represent the amount of volatile solids in the feedstock and digestate respectively.

The following equations were used to obtain percentage of total solid (%TS) loss and percentage of volatile solids (% VS) loss.

$$\% \text{ TS} = (M_0 - M_1)/\text{Mo} \times 100 \quad \text{.....(3.11)}$$

Where M_0 = dry weight of feedstock entering into the reactor, (g)

$$M_0 = TW_0 \times TS_0 \quad \text{.....(3.12)}$$

TW_0: wet weight of solid wastes entering into the reactor, (g)

TS_0: percentage total solid of feedstock (%TS)

M1: dry weight of digestate extracting from reactor, (g)

$M_1 = TW_1 \times TS_1$ ..... (3.13)

TW_1: wet weight of digestate extracting from the reactor, (g)

TS_1: percentage total solid of digestate (%TS)

$\% VS = (N_0 - N1)/N_0 \times 100$ ..... (3.14)

where, N_0 = weight of volatile solids entering into the reactor, (g)

$N_0 = M_0 \times VS_0$ ..... (3.15)

VS_0: percentage volatile solid of feedstock (%TS)

N1: weight of volatile solid of digestate extracting from reactor, (g)

$N_1 = M_1 \times VS_1$ ..... (3.16)

VS_1: percentage volatile solid of digestate (%TS)

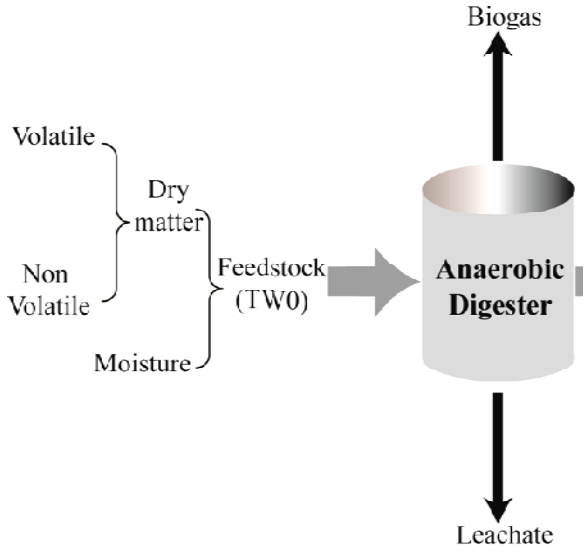


Figure 3.7 Material balance of anaerobic digestion system

d) Total Kjeldahl Nitrogen (TKN) Determination

Total Kjeldahl Nitrogen (TKN) is the sum of the organic nitrogen and the ammonia nitrogen forms in a sample. In the presence of sulphuric acid, potassium sulphate, and a mercuric sulphate catalyst (digestion reagent), the nitrogen, which is part of organic matter, is converted to ammonia by sodium thiosulfate and then distilled from alkaline solution.

Procedure

- Dry a sample of sludge in a drying oven at 103°C, grind thoroughly to a fine powder.
- Weigh approximately 1.0 g dried sample into a 500 ml kjeldahl digestion flask.
- Add 50 ml of digestion reagent and mix thoroughly.
- Place flask on digestion apparatus, heat slowly until frothing ceases and heat to boiling and continue boiling for 30 minutes until the liquid becomes clear.
- Cool the flask and dilute the sample with 350 ml of ammonia free distilled water.
- Add 0.5 ml phenolphthalein indicator.
- Tilt the digestion flask and carefully add a sufficient amount of sodium hydroxide - thiosulfate reagent to form an alkaline layer (pink zone) in the bottom of the flask.
- Connect the flask to the distillation apparatus, mix thoroughly and distil 200 ml of distillate into a boric acid absorbing solution.
- Determine Total Kjeldahl Nitrogen as ammonia using UV spectrophotometer (HITACHI, U-2900 UV/VIS spectrophotometer).

3.7.2 Leachate Characteristics Analysis

a) pH measurements

The pH was measured using digital PH meter (μpH system 362). The system measures and displays pH simultaneously. The pH meter was calibrated using buffer of pH 4.2, 7 and 9.

c) Volatile Fatty Acids and Alkalinity measurements

Alkalinity measurements are extensively used to judge the general conditions of the anaerobic reactor. Alkalinity and total volatile fatty acids (VFA) concentration in the anaerobic digesters were estimated using simple titration method (Anderson and Young, 1992).

Procedure:

Measurements were made done immediately after collecting the sample in mille equivalent/litre. About 50 ml of sample was taken in a beaker with stirrer bead and placed over a magnetic stirrer. Immediately pH was noted and the sample was titrated with 0.1N sulphuric acid, till pH reading is 5.1, noted the burette reading as V_1. Titration continued till pH becomes 3.5 and noted the reading as V_2. Calculated VFA (volume acid in mille equivalent/litre) and alkalinity (in mille equivalent/litre) using the following formula:

$A_1 = V_1 \times N \times 1000 / S$

Where, S = sample volume in ml,

N = normality of the acid

$A_2 = V_2 \times N \times 1000 / S$

Where, V_1, V_2 = volumes of acid required to reduce the pH to 5.1 to 3.5 respectively

Volatile acid in meq /l = $(M_4 \times M_2 - M_1 \times M_0)/-\Delta$

Alkalinity in meq /l = $(M_4 \times M_3 - M_5 \times M_1)/\Delta$

where $\Delta = 2.429 \times 10^8$

$M_0 = 1.162 \times 10^5$

$M_1 = 3.131 \times 10^4$

$M_2 = 3.156 \times 10^3$

$M_3 = 2.939 \times 10^3$

$M_4 = A1 / 10^{-5.1} - 10^{-pH}$

$M_5 = A1 / 10^{-3.5} - 10^{-pH}$

Where, pH = initial pH of the sample

d) COD analysis

The Chemical Oxygen Demand (COD) tests were carried out according to the open reflux method described in the standard methods for the examination of water and waste water, 20th edition, 1998 (APHA). Apparatus used was COD digester 2015M (Spectra lab)

Principle

Chemical Oxygen Demand (COD) test determines the oxygen demand for chemical oxidation of organic matter with the help of strong chemical oxidant. The organic matter gets oxidized completely by the potassium dichromate ($K_2Cr_2O_2$) in the presence of concentrated sulphuric acid to produce CO_2 and H_2O. The excess potassium dichromate remaining after the reaction is treated with Ferrous Ammonium Sulphate $[(FeNH_4)_2(SO_4)_2H_2O]$ the volume of dichromate consumed gives the oxygen required for oxidation of the organic matter.

Procedure

- Take 20 ml of the sample in a refluxing flask.
- Add 20 ml of $K_2Cr_2O_7$ and 30 ml of concentrated H_2SO_4
- Keep the flask in COD digester for about 1.5 hours.
- Add 30 ml of distilled water after digestion.
- Cool the flask and add 2-3 drops of ferroin indicator.
- Titrate against ferrous ammonium sulphate.
- The end point is the first sharp colour changes from blue green to reddish brown.
- Simultaneously, a distilled water blank, which was run along with the sample in similar way, as used as blank.

Calculation

Molarity of ferrous ammonium sulphate (FAS) solution = $$\frac{V_A * Molarity\ of\ K_2Cr_2O_7}{V_F}$$

Where,

V_A---Volume of reagent ($K_2Cr_2O_7$)

V_F---Volume of FAS used for titrating cold sample.

COD as mg O_2/ litre = (A-B) * M* 8000 / ml sample

Where, A = ml of FAS used for blank

B = ml of FAS used for sample

M = Molarity of FAS

e) Ammonia nitrogen

Ammonia is produced by the microbiological activity of organic nitrogenous matter. Ammonia produced a yellow coloured compound when reacted with alkaline Nessler's reagent. Photometry measurement measures the absorbance in a spectrophotometer. Apparatus used for the determination of ammonia nitrogen was UV spectrophotometer (HITACHI, U-2900 UV/VIS spectrophotometer).

Procedure:

- Prepare calibration curve using standards prepared from the stock solution (NH_4Cl-1000 ppm).
- Take 50 ml of sample or 50 ml of diluted sample with ammonia free water and add 1-2 drops of EDTA and 2 ml Nessler's reagent to this sample.
- Take the absorbance and calculate the concentration of NH_3-N from the calibration curve.

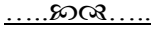
f) Total organic carbon

Total organic carbon (TOC) was calculated using total organic carbon analyser, Shimadzu TOC-LCPH E200. NPOC (Non- Purgeable Organic Carbon) method was used for calculating TOC.

Principles of NPOC

After acidifying the sample to pH 2 to 3, spurge gas is bubbled through the sample to eliminate the inorganic carbon component. The remaining total carbon is measured to determine total organic carbon, and

the result is generally referred to as TOC. NPOC stands for non purgeable organic carbon and refers to organic carbon that is present in a sample in a non-volatile form.



Chapter 4

RESULTS AND DISCUSSION

Contents

4.1 Introduction

The results and discussion chapter has been divided into three sections. In the first section, performance of batch anaerobic digesters for the treatment of OFMSW at room temperature and at different substrate concentration (TS concentration 83 g/l, 99 g/l and 115 g/l) has been discussed. Kinetic study and optimization using RSM are also discussed in this section. In the next section, performance of batch semi- dry anaerobic digestion of OFMSW at thermophilic temperature is discussed. The last section describes the results obtained during the bench scale anaerobic digestion of OFMSW. In this experiment, optimization of bench scale reactor treating OFMSW was performed by testing different OLRs. The study was started with a start-up phase (batch mode of operation) followed by continuous operation. In continuous operation, effect of various OLRs on the stability and performance of the reactor was evaluated at a constant retention time. The results have been discussed in the following sections.

4.2 Batch Study of OFMSW at Mesophilic Temperature

4.2.1 Feed Stock Characteristics

The OFMSW used in this experiment was composed of four different types of waste that are mixed to simulate the municipal solid waste composition used in this study. The composition of the substrate is given in the Table 3.1. Zeshan (2012) used similar simulated composition of municipal solid waste for anaerobic digestion. The summary of the characterization of substrate and reactor feeds is shown in Table 4.1. The weight of substrate used in the reactors R1, R2 and R3 were 700 g, 600 g and 500 g (wet weight) respectively.

Table 4.1 Characteristics of the substrate and feed

Parameter	OFMSW	R1	R2	R3
pH	6.15	6.42	6.75	6.64
TS (%)	18.5	12.32	10.5	9.4
VS (%)	89.6	85.37	84.5	86.6
VFA(meq /l)	10.85	8.65	9.57	6.98
COD (mg/l)	42835	41152	37318	31987
TKN (g/l)	1.05	1.1	1.09	0.85
TOC (g/l)	20.32	23.87	20.5	16.76

4.2.2 Performance of Batch Reactors

The experiments were carried out for 100 days at room temperature, 32°C (mesophilic digestion) at three different initial substrate concentrations of 115 g/l, 99 g/l and 83 g/l respectively. The experiments were concluded when there was no significant variation of cumulative biogas production.

The profile of pH and volatile fatty acids for the batch study are shown in the Figures 4.1 to 4.3. In an anaerobic system, the acetogenic

bacteria convert organic matter to organic acids, possibly decreasing the pH, reducing the methane production rate and the overall anaerobic digestion process unless the acids are quickly consumed by the methanogens. pH in the range of 6.8 to 7.4 should be maintained in the anaerobic digestion process, which is the optimum range for methanogens growth (Velmurugan B and Alwar Ramanujan, 2011). A decrease in pH was observed during the first few days of digestion due to the high volatile fatty acids formation; hence the pH was adjusted to 7 using 6N NaOH solution.

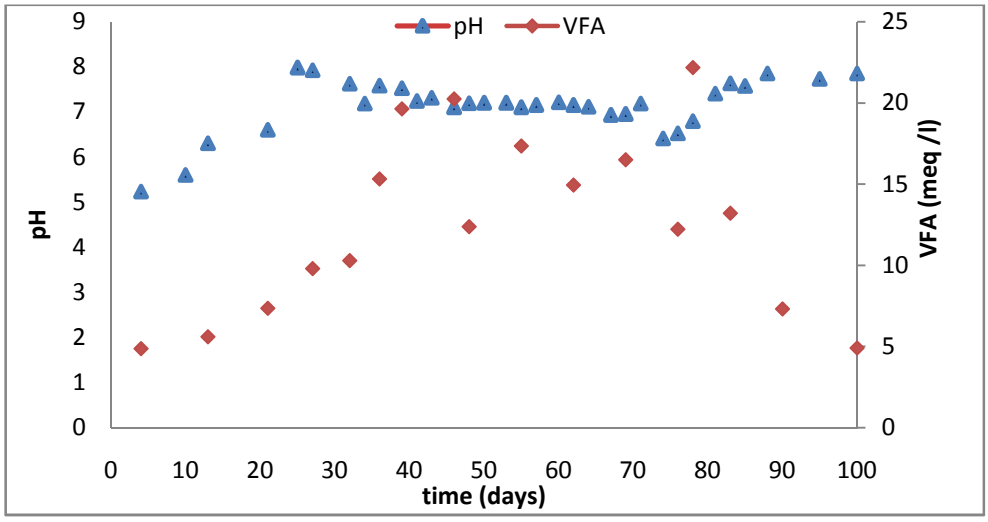


Figure 4.1 Variation of pH and VFA for TS concentration 115 g/l

From day 35 to 70, the pH was almost found steady. Despite of steady pH the biogas production was low during that period due to lack of mixing. The VFA generation in the beginning was high due to higher acidogenesis and lower methanogenic activity. The initial pH drop and high volatile fatty acid concentration show that the substrate contains some easily biodegradable constituents. After day 40, the VFA concentration was found

decreased due to methanogenic activity in which the intermediate organic acids was started to convert into biogas.

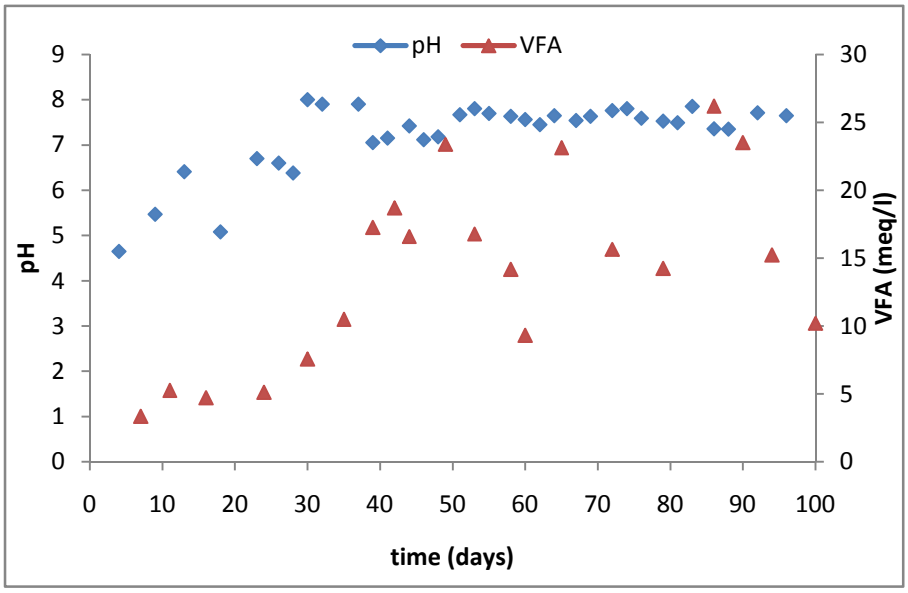


Figure 4.2 Variation of pH and VFA for TS concentration 99 g/l

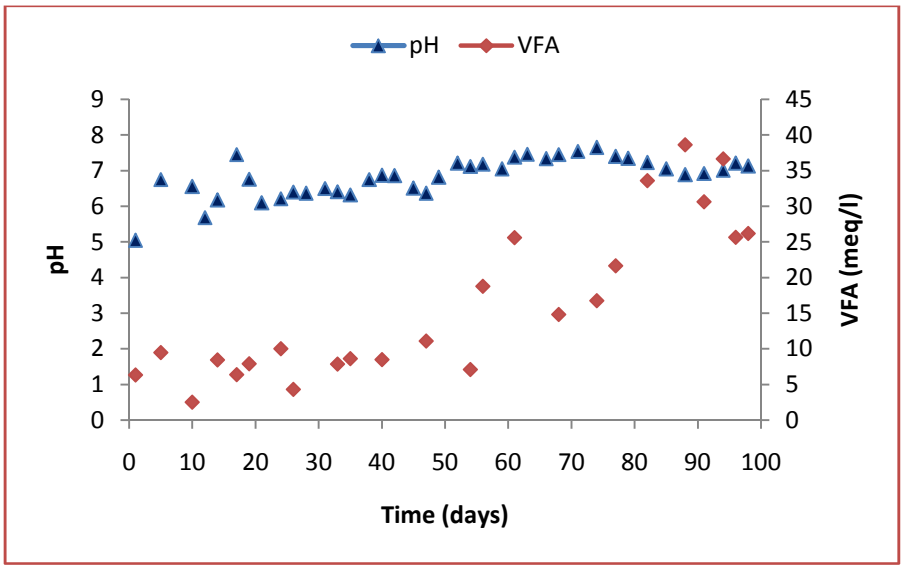


Figure 4.3 Variation of pH and VFA for TS concentration 83 g/l

Figure 4.4 to 4.6 depicts the variation of COD and NH_3-N during the study. The COD of the leachate was found decreasing due to conversion of organic matter into biogas. In this experiment, concentration of NH_3-N was increasing due to release of ammonia during hydrolysis of protein or utilisation of nitrogen for biomass synthesis. It is evident that NH_3-N concentration (>6000 mg/l) indicates the inhibition of methanogens in an acclimated environment (Mata-Alvarez et al., 2000). In this study, the NH_3-N concentration increased from 12 mg/l to 1400 mg/l. So it can be concluded that there is no inhibition of ammonia nitrogen during the AD process of this system.

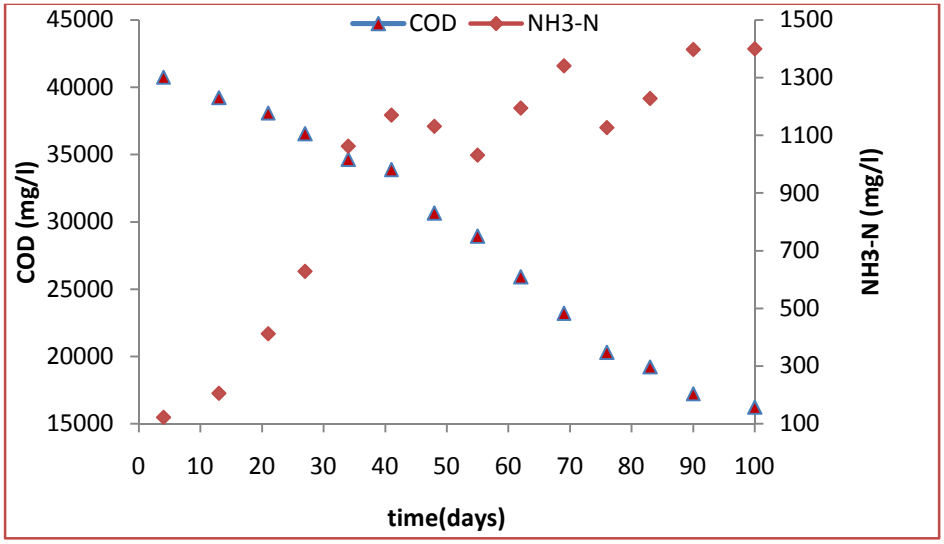


Figure 4.4 Evolution of COD and NH3-N (mg/l) in the digester for TS concentration115 g/l

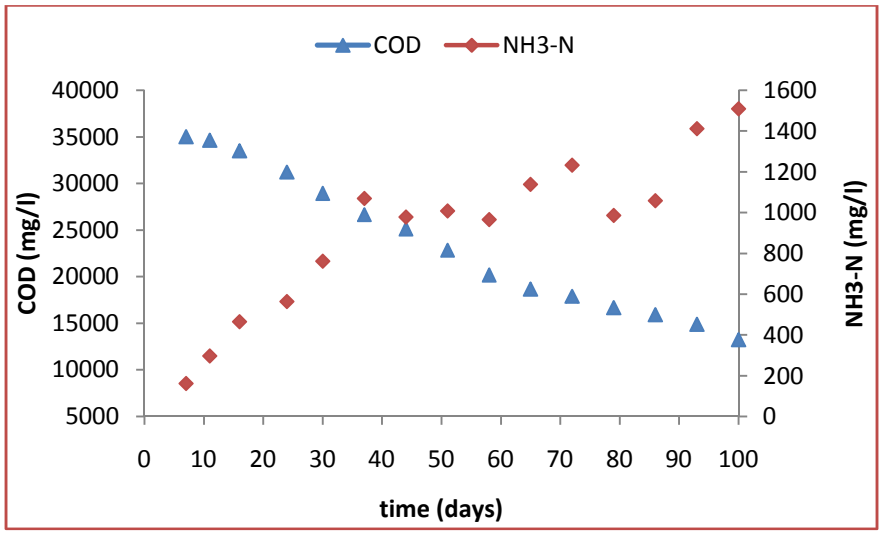


Figure 4.5 Evolution of COD and NH_3-N (mg/l) in the digester for TS concentration 99 g/l

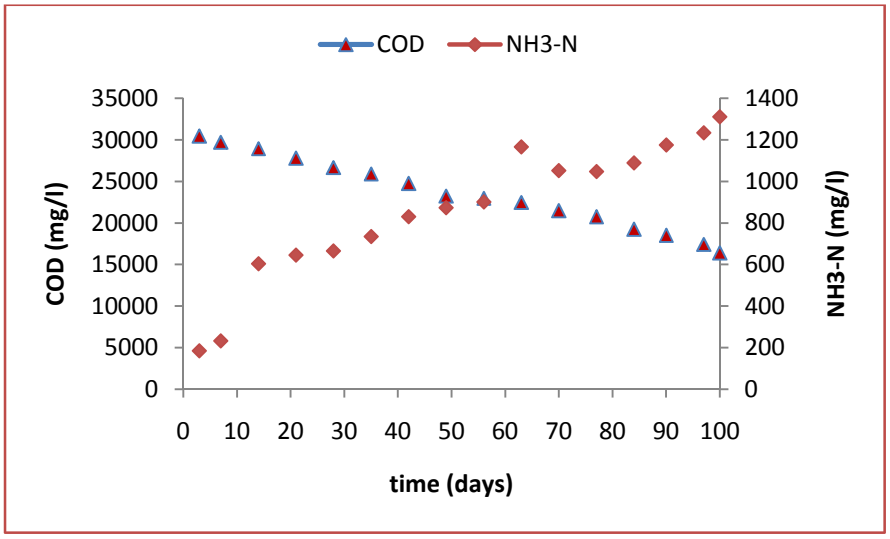


Figure 4.6 Evolution of COD and NH_3-N (mg/l) in the digester for TS concentration 83 g/l

Daily and cumulative biogas productions for 3 reactors are indicated by Figure 4.7 and 4.8 respectively, where the biogas production is high in

the beginning which was due to the entrapped air inside the reactor and the waste itself. The reactors R1, R2 and R3 were operated with total solid concentration of 115 g/l, 99 g/l and 83 g/l. Initially in the reactors R1 and R2, the biogas production was stopped due to the reduction of pH. So after adjusting the pH value in the optimum range by addition of 6N NaOH to the system, the production was increased. In reactor 3 optimum range of pH was initially made up, hence the biogas production was not stopped in R3. In R1 initially thick slurry was formed due to high solid contents in the reactor. So the production of biogas was reduced in the initial stages. The maximum daily biogas production obtained for R1 was 120 ml in 69th day and that for R2 and R3 were 340 ml in 58th day and 180 ml in 29th day. At the end of the 100 days digestion total cumulative biogas for R1, R2 and R3 were obtained as 3.574 L, 7.474 L and 4.957 L respectively. The biogas production was decreased from 85-100 days due to lack of amount of substrate.

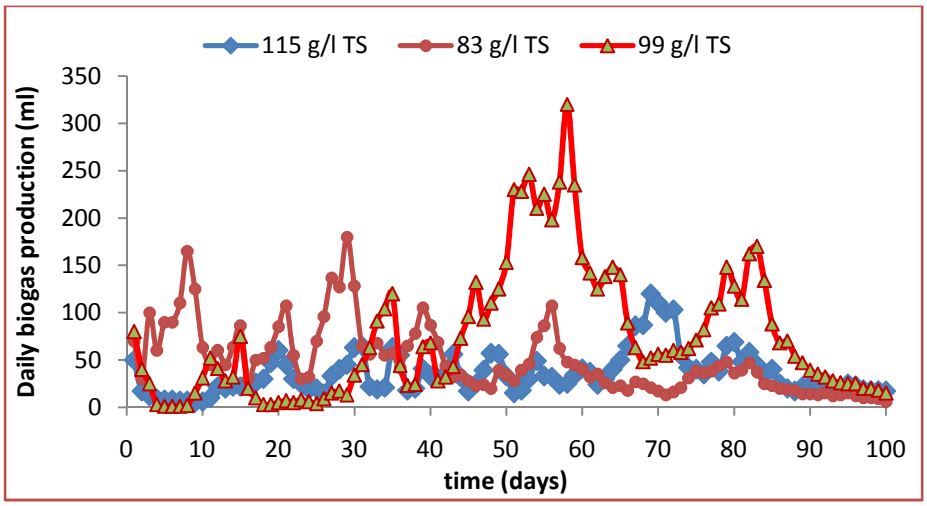


Figure 4.7 Variation of daily biogas production versus days for different substrate loading

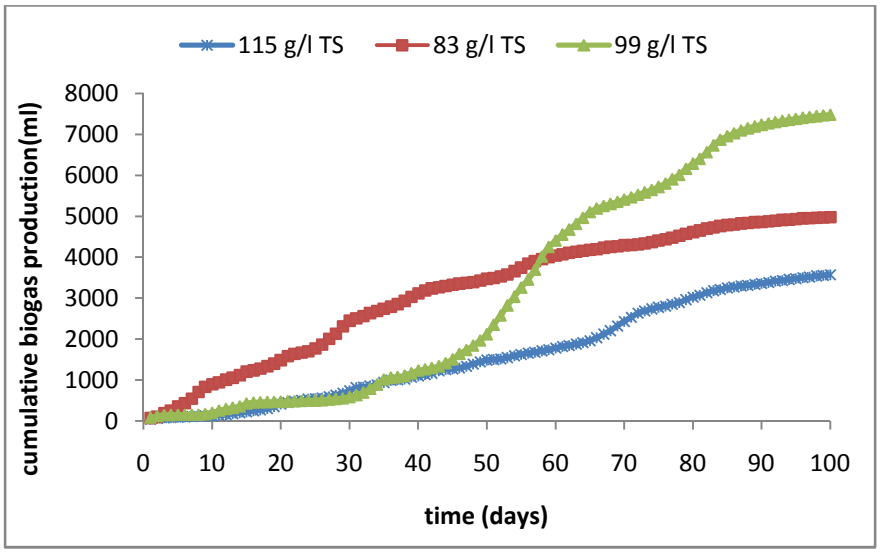


Figure 4.8 Variation of cumulative biogas production versus days for different substrate loading

4.2.3 Comparative Process Efficiency

The summary of performance of batch reactors mentioning the characteristics of initial and digested substrate, along with their degradation percentages, under different TS conditions of 115 g/l, 99 g/l and 83 g/l are given in Table 4.2.

Table 4.2 The summary of performance of batch reactors

Parameter	R1			R2			R3		
	Initial	Final	Degradation (%)	Initial	Final	Degradation (%)	Initial	Final	Degradation (%)
TS (g)	184	151.3	17.8	158.4	94.7	40.2	132.8	88.4	33.4
VS (g)	157.1	125.4	20.2	133.8	73.3	45.2	115.0	72.2	37.3
COD (g)	65.84	42.27	35.8	59.7	21.0	64.8	51.2	27.8	45.7
TKN (g)	1.76	1.63	7.4	1.74	1.42	18.4	1.36	1.22	10.3
TOC (g)	38.2	28.7	24.9	32.8	17.2	47.6	26.8	16.8	37.3

It is observed that 20.2 % of the total volatile matter was converted in reactor 1 and that for R2 and R3 were 45.2% and 37.3% respectively. From the Table 4.2, it is observed that maximum degradation was occurred for reactor 2. The biogas yield, biogas produced per kg volatile solids fed, for different concentrations of organic loading over 100 days digestion time at room temperatures is shown in Figure 4.9. The rates of biogas production differed significantly according to the organic loading. It can be observed from Figure 4.9 that bulk of substrate degradation takes place up to a period of approximate 80 days suggesting that the digesters should preferably be run at a digestion time close to 80 days for optimum biogas yield. At the end of the 100 days digestion, the biogas yields at TS concentration of 115 g/l, 99 g/l and 83 g/l were 22.7 L/kg VS, 55.9 L/kg VS and 43.1 L/kg VS respectively. These values are comparable with the values obtained by M. S. Rao and S. P. Singh (M. S. Rao and S. P. Singh, 2004). C: N ratio is most often used to indicate both the stability of organic matter and the quality of the digested substrate for its further use. In this study, C: N ratio of digested substrate was in the range 12:1–17:1,which is considered to be stable and high quality compost (Molnar and Bartha, 1988). However, the effluent chemical oxygen demand concentration indicates that it should be treated before using it for other applications.

From the results obtained, it can be concluded that digesters should preferably be run at 99 g /l (TS) at room temperature, since maximum biogas production was obtained at this total solid concentration.

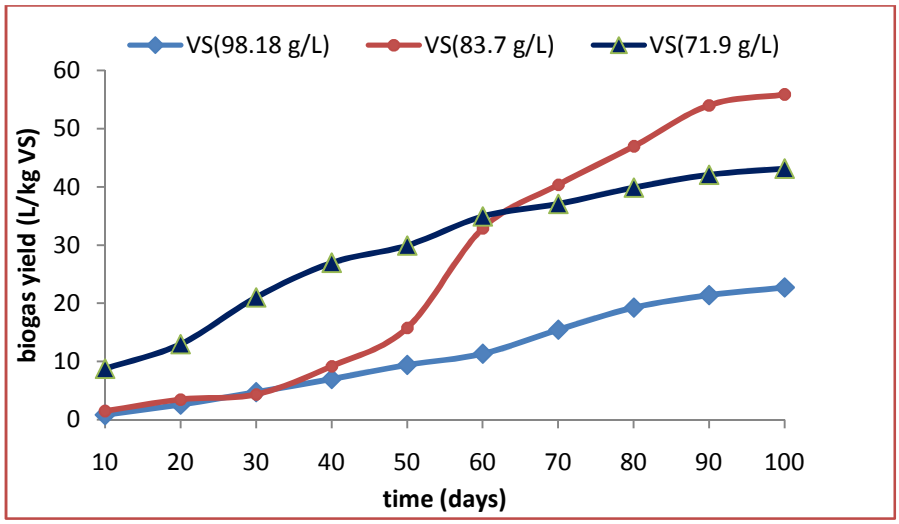


Figure 4.9 Biogas yield at different organic loading

4.2.4 Kinetic Study

Kinetic studies of anaerobic digestion process are useful to predict the performance of digesters. Detailed procedure is explained in the section 3.4.3. The cumulative biogas production at total solids concentration of 115 g/l, 99 g/l and 83 g/l maintained at mesophilic temperature (32 ºC) along with the predicted value using the first-order kinetic model described by equation 3.4 are shown in Figures 4.10 -4.12. The values G_∞ and k were obtained from a non-linear regression analysis using Curve Expert 1.4.

It has been observed that the cumulative biogas production was fit well with the first-order kinetic model as is evident from the correlation coefficient between the experimental and predicted value (Table 4.3). The values of kinetic constants for R1, R2 & R3 were calculated from the Figures 4.13, 4.14 & 4.15 respectively. The values of kinetic constants (k) obtained for R1, R2 & R3 were 0.0196, 0.0292 and 0.0319 (day^{-1}) respectively. These values are comparable

with the values obtained by M. S. Rao and S. P. Singh (M. S. Rao and S. P. Singh, 2004). The summary is given in Table 4.3.

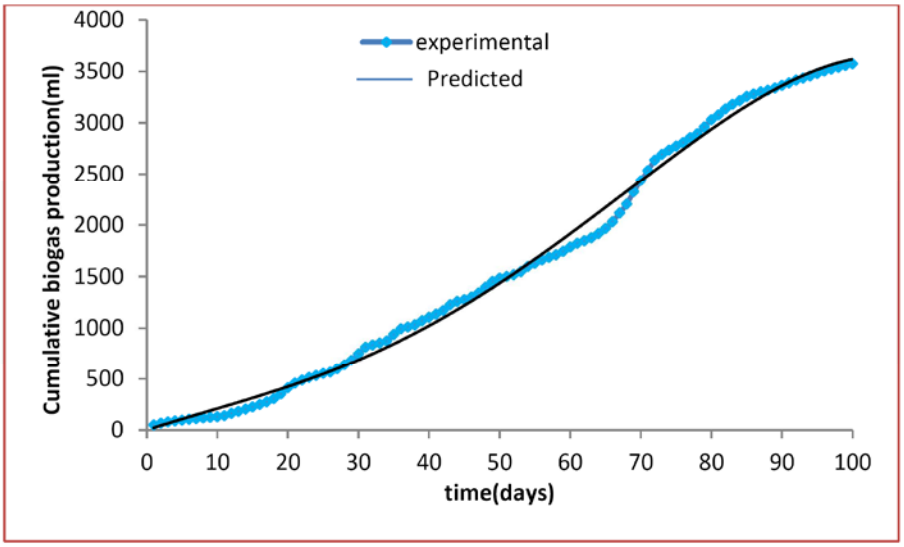


Figure 4.10 Cumulative biogas productions (TS concentration 115 g/l)

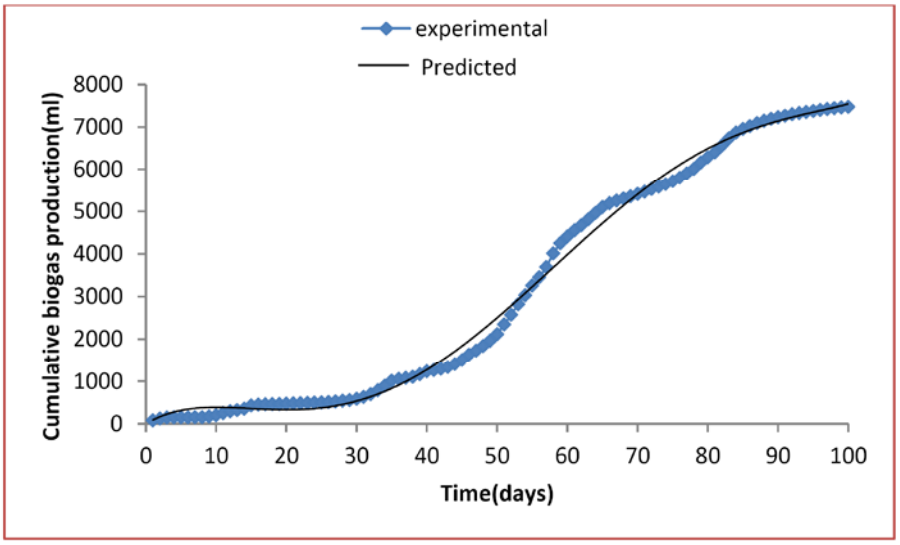


Figure 4.11 Cumulative biogas production (TS concentration 99 g/l)

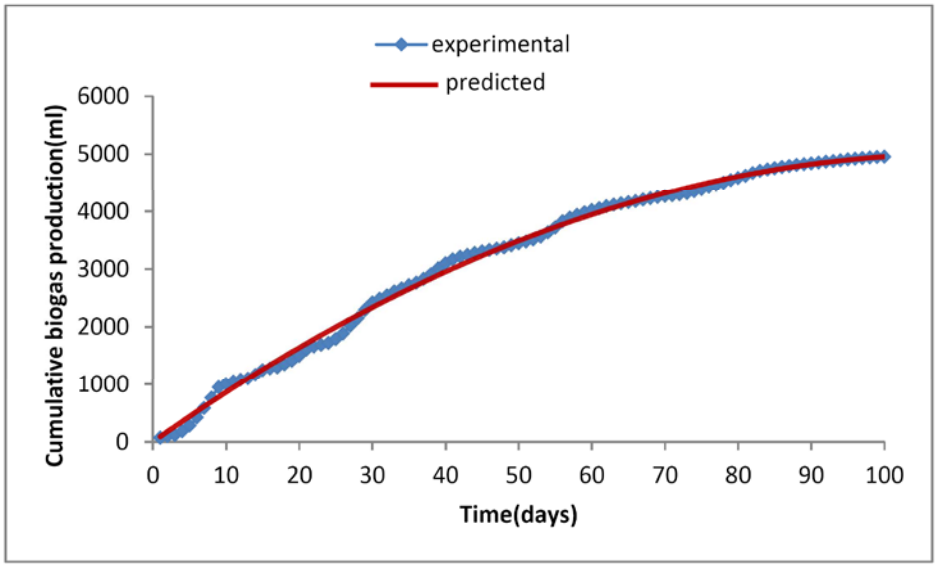


Figure 4.12 Cumulative biogas production (TS concentration 83 g/l)

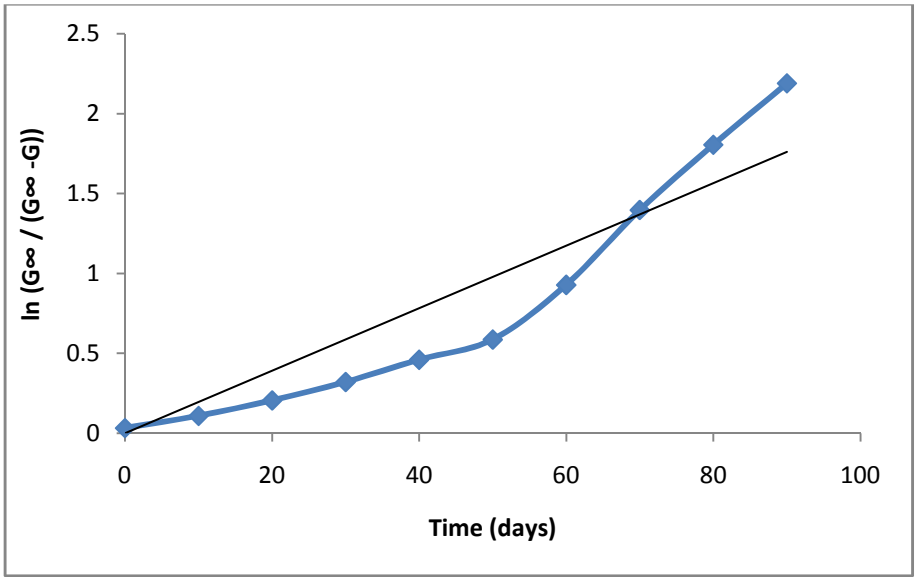


Figure 4.13 Plot for the determination of k for TS concentration of 115 g/l

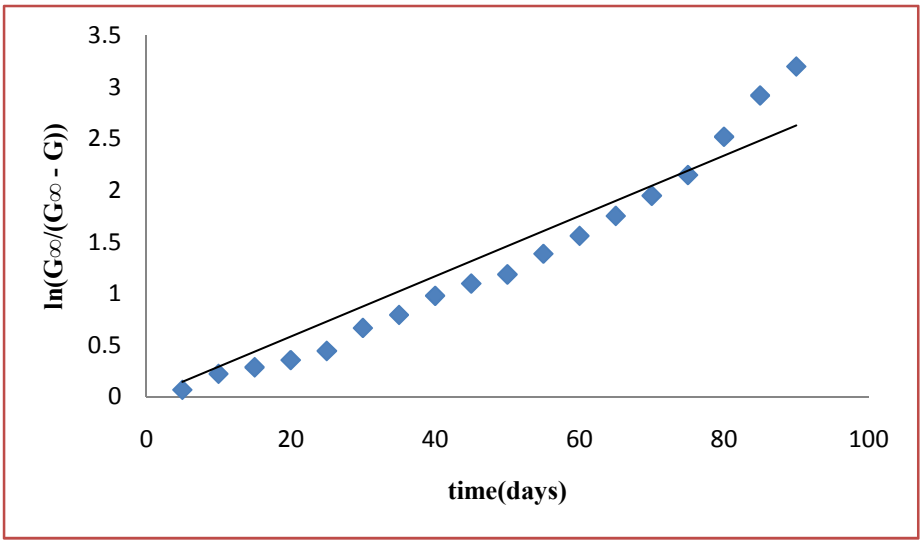


Figure 4.14 Plot for the determination of k for TS concentration of 99 g/l

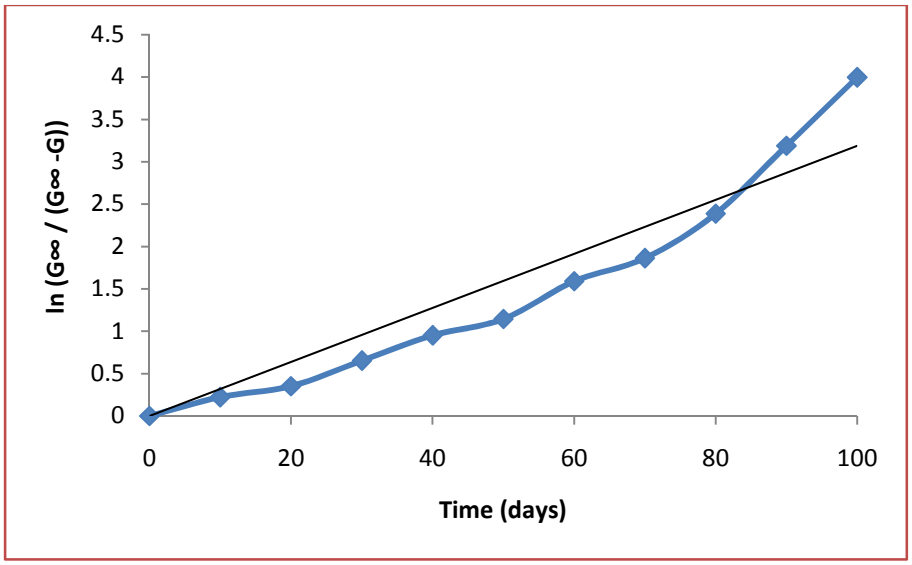


Figure 4.15 Plot for the determination of k for TS concentration of 83 g/l

Table 4.3 Values of fitting functions and statistical measures for the kinetic model

TS concentration (g/l)	Ultimate Biogas production G∞ (ml)	Biogas production rate constant k (day^{-1})	Correlation Coefficient (R^2)
115	4025	0.0196	0.8684
99	7540	0.0292	0.929
83	5050	0.0319	0.9076

4.2.5 Optimization of Batch Study

4.2.5.1 Optimization of Biogas Production

In this study, optimization of process controlling factors was done by Response Surface Methodology (RSM). RSM is a statistical technique for analysing the effects of several independent variables on the responses (Zinatizadeh et.al., 2006). The objective of this study was to investigate the effects of initial pH, substrate concentration and total organic carbon on biogas production from OFMSW. Preliminary work carried to fix a range of independent variables is explained in section 4.2. Stat-Ease software with Design Expert v.8 was used to analyse the effects of variables individually and their interactions to determine their optimum level. The point prediction method was used for optimization of the levels of each variable for maximum response. The optimal levels for the independent variables and the effect of their interaction on biogas production were further explored using the central composite design (CCD) of RSM. The full experimental plans with respect to their actual and coded forms are listed in Tables 4.4 & 4.5.

Table 4.4 Coded value of independent variables and experimental ranges

Factor	Name	Coded lower limit	Coded Higher limit	Real lower limit	Real higher limit
A	Initial pH	-1	+1	6.00	7.00
B	Substrate Concentration (TS-g/l)	-1	+1	83.00	115.00
C	TOC (g/l)	-1	+1	16.76	23.87

Table 4.5 CCD matrix for three variables with actual biogas production

Run	Initial pH A	Substrate (TS-g/l) B	TOC(g/l) C	Biogas production (ml)	Biogas yield (L/kg VS)
1	6.50	99.00	20.32	7400	53.8
2	7.00	83.00	16.76	4500	37.8
3	7.00	115.00	16.76	3150	20.1
4	7.34	99.00	20.32	7450	54.2
5	6.50	115.00	20.32	3200	20.4
6	7.00	115.00	23.87	3400	21.6
7	6.00	83.00	16.76	4600	38.7
8	6.50	83.00	20.32	4800	40.3
9	6.50	99.00	20.32	7415	53.9
10	6.50	83.00	20.32	4820	40.5
11	6.00	115.00	16.76	3100	19.7
12	6.50	99.00	16.76	800	49.5
13	5.66	99.00	20.32	7000	50.9
14	6.00	83.00	23.87	4700	39.5
15	6.50	99.00	20.32	7380	53.7
16	6.50	99.00	20.32	7400	53.8
17	6.50	99.00	20.32	7415	53.9
18	6.50	99.00	20.32	7380	53.7
19	7.00	83.00	23.87	4800	40.3
20	7.00	115.00	23.87	3410	21.7

By applying multiple regression analysis on the experimental data, the second-order polynomial equation 4.1 was derived to explain the organic acids production.

$$\text{Biogas} = 7343.15+96.03A -759.30B +88.78\ C +69.28\ AB +81.78AC - 41.76BC - 26.52\ A^2 - 3241.51\ B^2 - 209.95C^2 \quad \text{..... (4.1)}$$

Where, A, B, C are the coded values for initial pH, substrate concentration and total organic carbon, respectively. The full experimental plan of CCD design for studying the effects of three independent variables, viz. initial pH (A), substrate concentration (B) and TOC (C) are listed in Table 4.5.The statistical significance of the second-order polynomial equation was checked by an F-test (ANOVA). The corresponding all the data are shown in Table 4.6.The Model F-value of 445.8 implies the model is significant. In addition, the ANOVA of the quadratic regression model demonstrated that the model was highly significant ($p < 0.05$) (Table 4.6). The linear model terms of initial pH (A) and substrate concentration (B) and the quadratic model terms of the substrate concentration (B^2) and TOC (C^2) were significant ($p < 0.05$), indicating that these two variables had an individual effect on biogas yield. However, the linear model terms of TOC was insignificant ($p > 0.05$), suggesting that there was no linear effect of this variable on biogas yield. The interactive effects for all of these factors were found to be insignificant ($p > 0.05$) (Table 4.6). Additionally, the experimental biogas production was close to the predicted value using equation 4.1 (Figure 4.16).

Table 4.6 Regression analysis for the production of biogas for quadratic response surface model fitting (ANOVA)

Source	Sum of Squares	Degree of freedom	Mean Square	F Value	p-value Prob > F	
Model*	5.717E+007	9	6.496E+006	445.80	< 0.0001	Significant
A-Initial pH	5.846E+007	*1*	*93395.21*	*6.41*	*0.0298*	
B-Substrate Concentration (TS)	*93395.21*	*1*	*4.736E+006*	*324.99*	*< 0.0001*	
C-TOC	*4.736E+006*	*1*	*47296.67*	*3.25*	*0.1018*	
AB	*47296.67*	*1*	*24097.24*	*1.65*	*0.2274*	
AC	*24097.24*	*1*	*33577.45*	*2.30*	*0.1600*	
BC	*33577.45*	*1*	*9899.15*	*0.68*	*0.4290*	
A2	*9899.15*	*1*	*9608.27*	*0.66*	*0.4357*	
B2	*9608.27*	*1*	*3.030E+007*	*2079.35*	*< 0.0001*	
C2	*3.030E+007*	*1*	*1.111E+005*	*7.62*	*0.0201*	
Residual	1.457E+005	10	14571.16			
Lack of Fit	*1.444E+005*	*4*	*36107.07*	*168.81*	*< 0.0001*	*Significant*
Pure Error	*1283.33*	*6*	*213.89*			
Cor Total	5.861E+007	19				

* SD=120.71; Mean = 5506.00; R-Square = 0.9975; Adj R-Squared = 0.9953; C.V.%=2.19; Pred R-Squared = 0.9169; PRESS = 4.870E+006; Adeq Precision = 52.185

For biogas production, the correlation coefficient (R^2) of polynomial equation was found as 0.9975. The R^2 value indicated a measure of variability in the observed response values which could be described by the independent factors and their interactions over the range of the corresponding factor. This implied that the sample variation of 99.75% of the total variation could be explained by the model and only 0.25% of it was not explained by the model. So, quadratic model was chosen for this analytical work.

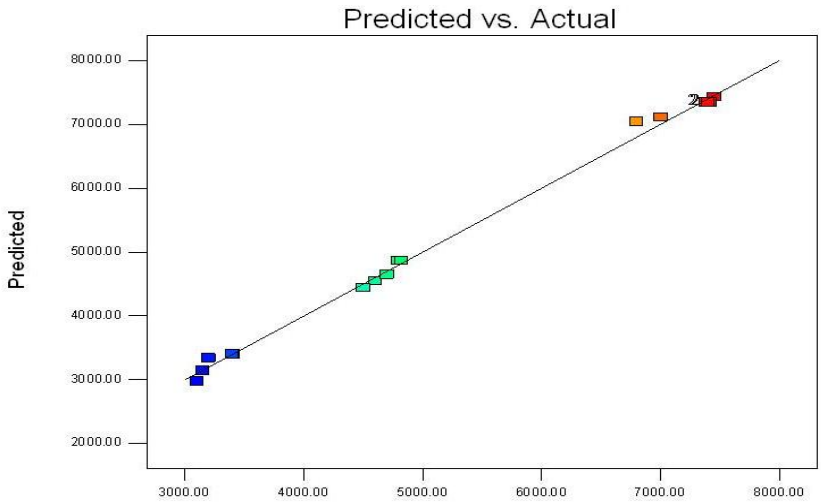


Figure 4.16 Predicted vs. experimental biogas values

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio found here is 52.185 which indicated an adequate signal for this study. This model was used to navigate the design space. The adjusted R^2 was also very high, which indicated the higher significance of the model. The "Pred R-Squared" value of 0.9169 showed the reasonable agreement with the "Adj R-Squared" value of 0.9953. This indicated a good agreement between the observed and the predicted values. The percentage of coefficient of variation (CV %) is a measure of residual variation of the data relative to the size of the mean. Usually, the higher the value of CV, the lower is the reliability of experiment. Here a lower value of CV (2.19 %) indicated a greater reliability of the experiment. The Predicted Residual Sum of Squares (PRESS) was a measure of how well the model fitted each point in the design. The smaller the PRESS statistics, better would be the model fitting the data points. Here the value of PRESS found as 4.870E+006. Moreover the "Lack of Fit F-value" of 168.81 implies that

Lack of Fit is significant. There is only a 0.01% chance that a "Lack of Fit F-value", this large could occur due to noise. The model showed standard deviation and mean values of 120.71 and 5506.00, respectively.

Graphical representations of the response surface are shown in Figures 4.17 and 4.18; to view the effects of initial pH, Substrate concentration and TOC on biogas production. Figure 4.17 represents the 3D surface plot. The contour plots (Figure 4.18) determined the interaction of the process parameters and optimum value of each component for maximum response. Those plots were obtained from the pair-wise combination of the independent factors, while keeping other factors at its centre point level. Figure 4.17 (a) & 4.18 (a) shows the effect of substrate concentration, initial pH and their interactive effects on biogas yield with the optimum level of TOC (20.32).The optimum values of the substrate concentration and initial pH for biogas yield is indicated at the top of the surface [Fig.4.17 (a)]. The biogas yield increased with increase in the substrate concentration from 89 to 107 g/l when the initial pH and TOC kept at their centre values. The maximum biogas production of 53.9 L/kg VS was obtained with substrate concentration of 99 g/l and initial pH 6.5 respectively. The effects of TOC, initial pH and their interactive effects, with optimum level of substrates concentration (99 g/l) on biogas yield were shown in Figure 4.17 (b) & 4.18(b). Figure 4.17(c) and 4.18 (c) show the effects of substrate concentration, TOC and their interactive effects on biogas yield with the optimum level of pH (6.5). It was found that biogas yield increased with increase in substrate concentration from 89 to 107 g/l. Highest biogas yield of 53.4 L/kg VS was obtained with an initial substrate concentration of 99 g/l. An inhibitory effect of high substrate concentration generally occurs in anaerobic digestion process, depending on the types of substrates and microorganisms.

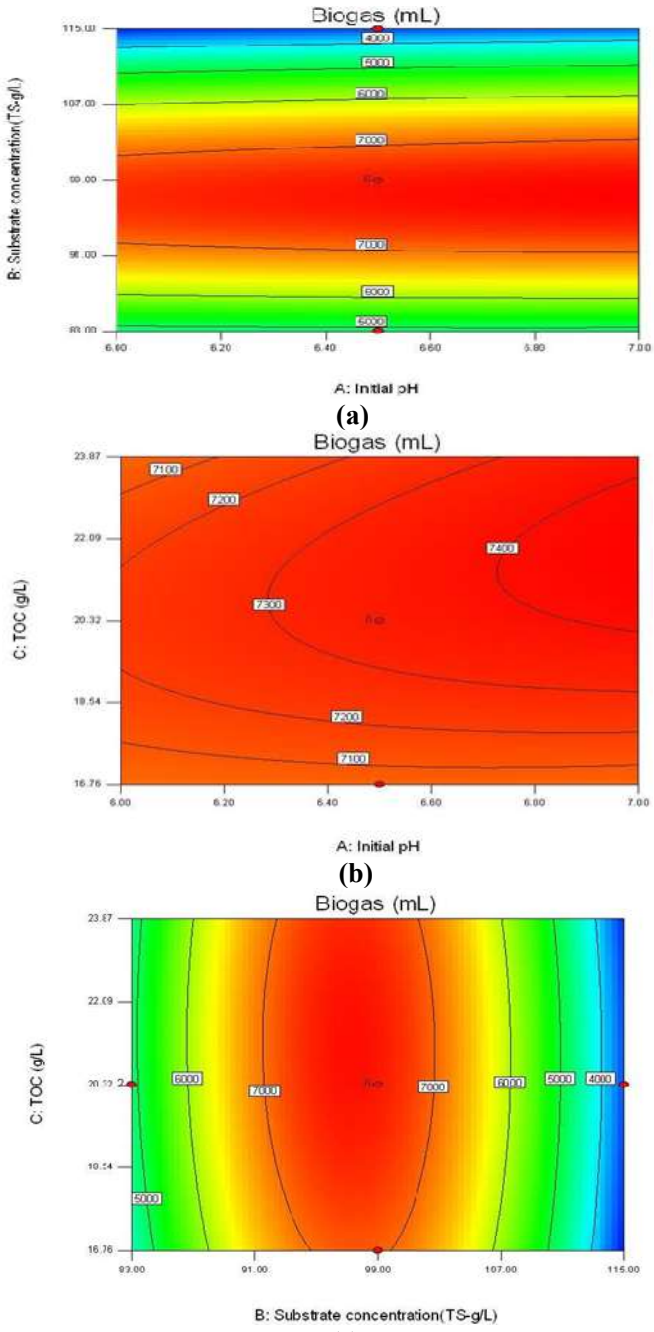


Figure 4.17 Contour plot of biogas production as a function of (a) Substrate concentration(B) and initial pH(A),(b) TOC (C) and Initial pH (A), (c) Substrate concentration(B) and TOC(C)

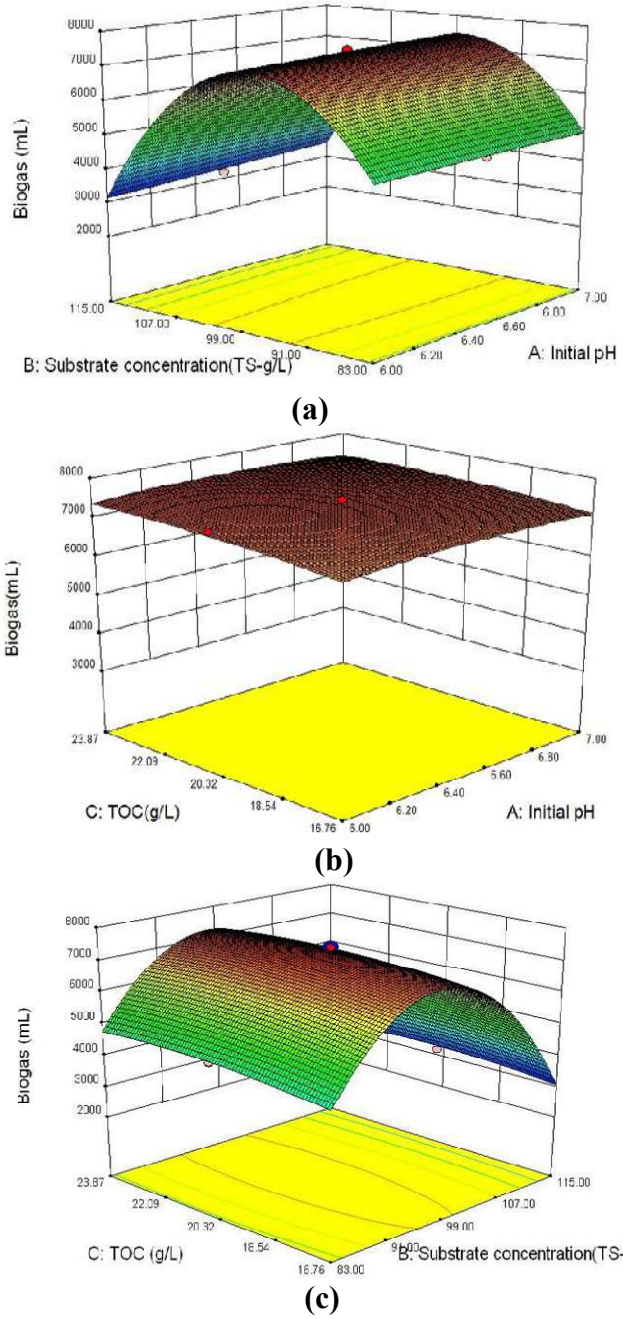


Figure 4.18 3D plot of biogas production (a) interaction between Substrate concentration(B) and initial pH(A),(b) interaction between TOC (C) and initial pH (A), (c) interaction between substrate concentration(B) and TOC(C)

The optimum conditions for maximizing the biogas yield calculated by the obtained model [eq. (4.1)] were a substrate concentration of 99 g TS/l, an initial pH of 6.5 and TOC of 20.32 g/l from point prediction method. Under the optimum conditions, the predicted maximum biogas yield of 53.4 L/kg VS was obtained from the quadratic regression model. The experimentally determined production values (Table 4.6) were close agreement with the statically predicted on, which confirm that the RSM with CCD analysis is a useful technique to optimize the biogas yield from the organic fraction of municipal solid waste through anaerobic digestion.

4.2.5.2 Conclusions

The present study focused on the optimization of process parameters such as substrate concentration, initial pH and TOC for the maximal biogas production. Optimization of those variables was carried out by Response Surface Methodology using Central Composite Design. Only the initial pH and substrate concentration had significant individual effects on biogas yield. The interactive effects for all of these factors were found to be insignificant ($p > 0.05$). The optimum conditions for maximizing the biogas yield were a substrate concentration of 99 g TS/l, an initial pH of 6.5 and TOC of 20.32 g/l. At this optimized condition, biogas yield was 53.4 L/kg VS. The maximum generation of biogas found experimentally using the optimized condition is 53.8 L/kg VS, which is in correlation with the predicted value (53.4 L/kg VS). It can be concluded that the RSM with CCD analysis is a useful technique to optimize the biogas yield from the organic fraction of municipal solid waste through anaerobic digestion. Hence, it is concluded from the present study that AD of OFMSW with substrate concentration of 99 g/l (TS-10.5%) is a semi-dry digestion. Therefore, next experiment is

done to study the performance of semi-dry digester under thermophilic condition.

4.3 Batch Study of OFMSW at Thermophilic Temperature

The objective of the present study was to investigate the performance of semi - dry anaerobic digestion of OFMSW in a single stage batch anaerobic reactor operated at thermophilic condition (50°C) with a substrate concentration of 100 g/l (TS-11.2%) and to study the kinetics.

4.3.1 Feed Stock Characteristics

The OFMSW used in this experiment was composed of four different types of waste that are mixed to simulate the municipal solid waste composition used in this study. The composition of the substrate is shown in the Table 3.1. The summary of the characterization of substrate and reactor feed is given in Table 4.7.

Table 4.7 Characteristics of the substrate and feed

Parameter	OFMSW	Feed
pH	6.20	6.61
TS (%)	18.7	11.2
VS (%)	90.6	87.8
VFA (meq/l)	10.85	10.57
COD (mg/l)	36936	38018
TKN (g/l)	1.04	1.06
TOC (g/l)	20.49	22.5

4.3.2 Performance of Batch Reactor

The experiment was carried out for 45 days at thermophilic condition (50°C). Biogas production is the primary indicator to evaluate the performance efficiency of the reactor. Figure 4.19 indicates the daily and cumulative

biogas production where the biogas production was high in the beginning which was due to the entrapped air inside the reactor. From Figure 4.19, it is clear that the biogas production was fluctuated during the first 11 days of operation and from day 12 to15, it increased and then decreased. This may be due to the reduction of pH. So after adjusting the pH value in the neutral range by addition of 6N NaOH to the system, the production was increased. From day 21 to 29 biogas production was increased sharply. The highest volume of biogas production (275 ml/day) was achieved at the same day. It is clearly seen that the volume of biogas increased with the operation time indicating the balanced reactor performance. At the end of the 45 days digestion total cumulative biogas obtained was 3520 ml. The biogas production was decreased towards the end of the digestion, this may be due to lack of substrate.

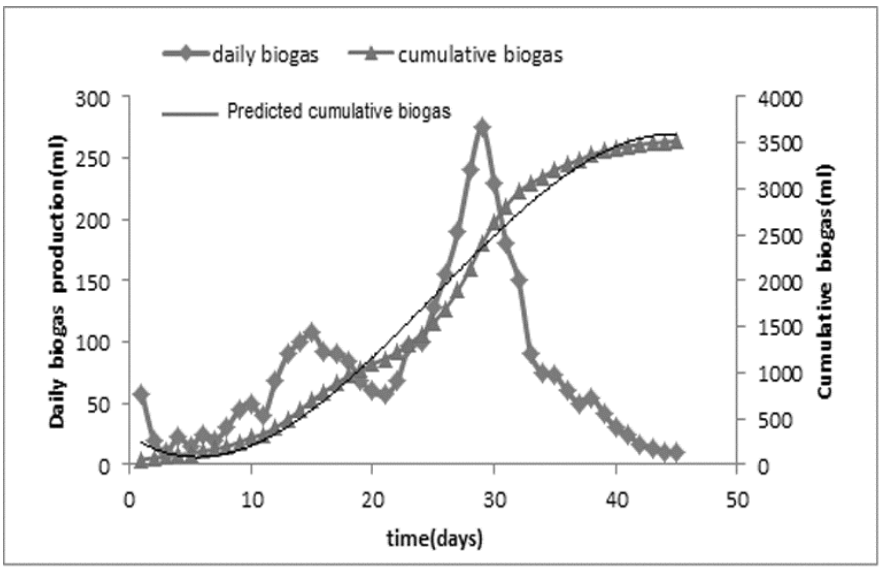


Figure 4.19 Variation of daily and cumulative biogas production versus days

In an anaerobic system, the acetogenic bacteria convert organic matter to organic acids, and then the value of pH is decreased. This result in a reduction of methane production rate this may be due to the accumulation of volatile fatty acid. pH in the range of 6.8 to 7.4 should be maintained in the anaerobic digestion process, which is the optimum range for methanogens growth (Velmurugan B and Alwar Ramanujan,2011). A decrease in pH was observed during the initial days of digestion (up to 10 days) this may be due to the high volatile fatty acids formation; hence the pH was adjusted to 7 using 6N sodium hydroxide solution. Figure 4.20 shows the variation profile of pH and Volatile Fatty Acid (VFA) concentration.

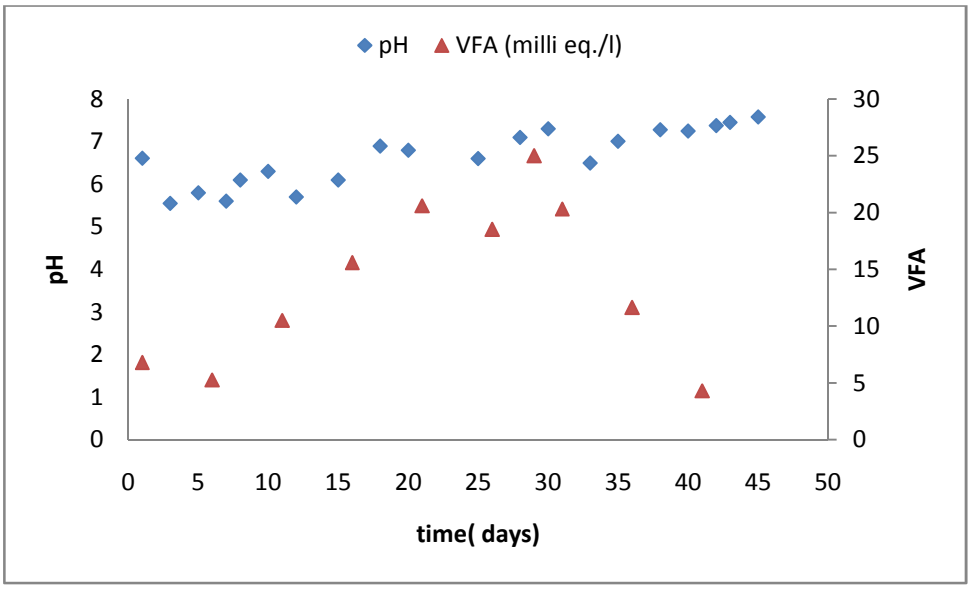


Figure 4.20 Variation of pH and VFA

The pH adjustment aided the system in starting up the process of methanogenesis. After that, pH was stabilized in the range of 7.0 - 7.6. The VFA generation in the beginning was high due to higher acidogenesis and

lower methanogenic activity. The initial pH drop and high volatile fatty acid concentration show that the substrate contains some easily biodegradable constituents. VFA concentration was increased till 29th day and then decreased. Maximum VFA concentration of 25.1 meq/l was observed on the same day. After that VFA concentration was found decreased due to methanogenic activity in which the intermediate organic acids were started to convert into biogas.

The Figure 4.21 depicts the variation of COD and NH_3-N during the study. The COD of the leachate was found decreasing due to conversion of organic matter into biogas. In this experiment, concentration of NH_3-N was increasing due to release of ammonia during hydrolysis of protein or utilisation of nitrogen for biomass synthesis. Ammonia nitrogen is an important parameter for the buffer capacity in an anaerobic reactor. With concentrations of up to 1000 mg/l, ammonia nitrogen stabilizes the pH value. Ammonia nitrogen is released during the anaerobic hydrolysis of protein, causing an increase of the pH value (Klaus Fricke et al., 2007). It is evident that NH_3-N concentration (>6000 mg/l) indicates the inhibition of methanogens in an acclimated environment (Mata-Alvarez et al., 2000). There was no large amount of ammonia nitrogen was extracted from the beginning of the digester. However, rapid increase of ammonia nitrogen occurred after three weeks for thermophilic digestion, and maintained high until the end of the experiment. In this study, the NH_3-N concentration increased from 250 mg/l to 1910 mg/l. So it can be concluded that there is no inhibitions of ammonia nitrogen during the AD process of this system.

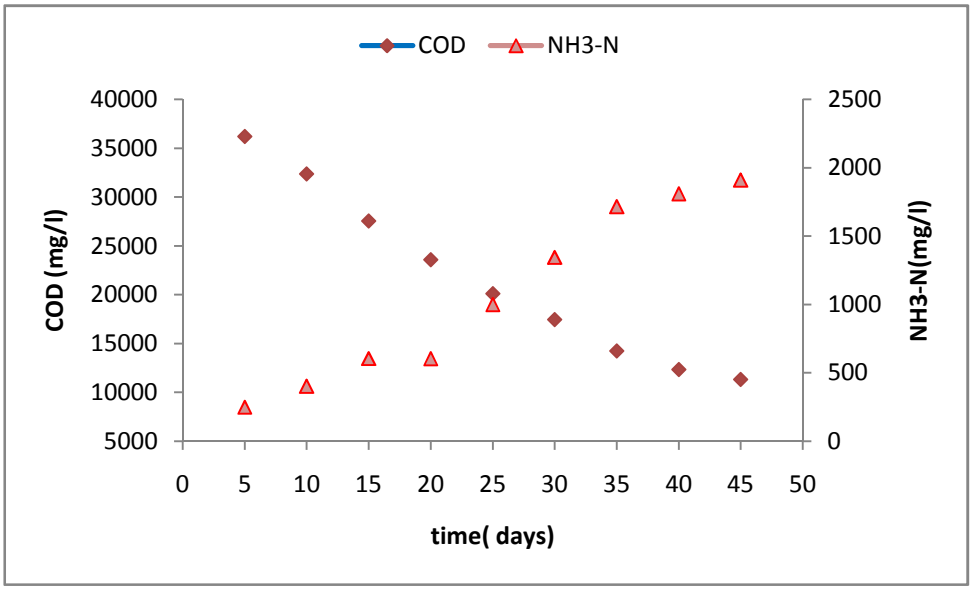


Figure 4.21 Evolution of COD and NH_3-N (mg/l) in the digester

The summary of performance of thermophilic batch reactor mentioning the characteristics of initial and digested substrate, along with their degradation percentages, is given in Table 4.8. It is observed that 66.7% of the total volatile matter in the substrate was converted during the digestion. The low C/N weight ratio in the digested substrate indicates that it can be utilized as bio fertilizer or soil conditioner. The biogas yield, biogas produced per kg organic solids (volatile solids) for the concentration of organic loading of 87.8 g/l (VS) over 45-days thermophilic digestion is shown in Figure 4.22. At the end of the digestion maximum biogas yield was 52.9 L/ kg VS.

Table 4.8 Summary of performance of thermophilic batch reactor.

Parameter	Initial	Final	Degradation (%)
TS (g)	80	30.64	61.7
VS (g)	70.24	23.39	66.67
COD(g)	30.42	9.08	70.15
TOC(g)	18	3.54	80.37
TKN(g)	0.848	0.649	23.5

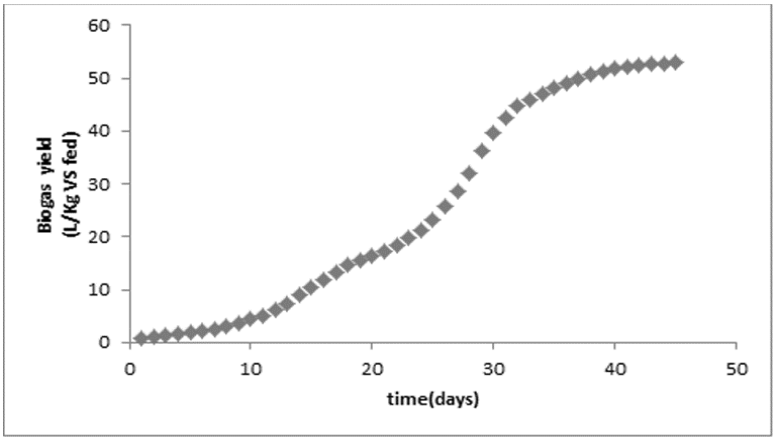


Figure 4.22 Biogas yield vs. time

4.3.3 Kinetic Study

Kinetic studies of anaerobic digestion process are useful to predict the performance of digesters. Detailed procedure was explained in the section 3.4.3. The cumulative biogas production at total solids concentration of 100 g/l maintained at thermophilic temperature along with the predicted value using the first-order kinetic model described by equation 3.4 is shown in Figure 4.23. The values G_∞ and k were obtained from a non-linear regression analysis using Curve Expert 1.4. It has been observed that the cumulative biogas production was fit well with the first-order kinetic model

as is evident from the correlation coefficient between the experimental and predicted value. The regression coefficient and the ultimate biogas production were 0.9896 and 3608 ml respectively. The value of kinetic constant (k) for the thermophilic digestion was calculated from the Figure 4.23. The k value obtained as 0.0249 (day^{-1}).This value is comparable with the value obtained by M. S. Rao and S. P. Singh, 2004.

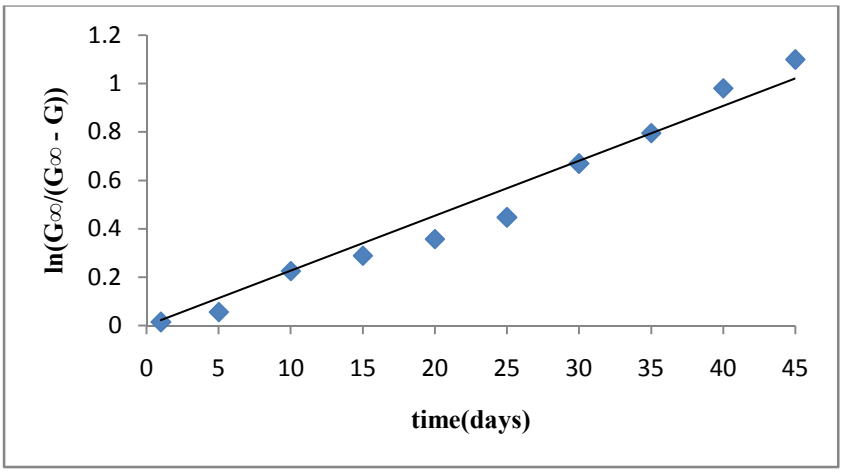


Figure 4.23 Plot for determination of kinetic constant (k)

4.3.4 Conclusions

The present study focused on the batch anaerobic digestion of OFMSW under thermophilic condition. At the end of the 45 days digestion the biogas yield was 52.9 L/kg VS for the TS concentration 100 g/l. The value of reaction rate constant, k, calculated for the reactor using first order kinetics was obtained as 0.0249 day^{-1}. It is observed that 66.7% of the total volatile matter in the substrate was converted during this semi-dry digestion. The low C/N weight ratio in the digested substrate indicates that it can be utilised as bio fertilizer or soil conditioner.

From the results, it is concluded that there was not much difference in biogas yield when compared with semi- dry batch mesophlilc digestion (32°C). In thermophilic AD, there is an accumulation of VFA and symptoms of failure due to high ammonia concentration. Hence bench scale study was done under mesophilic condition for semi-dry anaerobic digestion.

4.4 Bench Scale Study for Continuous Process

This section describes the results obtained during the bench scale semi-dry anaerobic digestion of OFMSW. In this experiment, optimization of bench scale reactor treating OFMSW was performed by testing different OLRs. The study was started with a start-up phase (batch mode of operation) followed by continuous operation. In continuous operation, effect of various organic loading rates on the stability and performance of the reactor was evaluated at a constant retention time. The results have been discussed in the following sections.

4.4.1 Reactor Start-up

The reactor was initiated with the fresh waste of 12 kg and 3.6 kg (30% of waste) of inoculum. The total and working volume of the reactor were 36.8 L and 29.4 L respectively. Homogenization of fresh wastes with inoculum was done properly before feeding into the system. Water was added to obtain the desired total solid concentration. TS concentration of the feed was 12%, hence it is a semi-dry AD process. The characteristics of feed and substrate are given in Table 4.9. To obtain a homogeneous suspension, leachate from the bottom of the reactor was recirculating by a peristaltic pump (Ener Tech) at the rate of 0.08 L/ min for 6 hours daily. The operating temperature in the start-up phase was in mesophilic range (32°C). In the first 50 days (start-up phase), the reactor was not fed.

Table 4.9 Characteristics of the substrate and feed during start- up of bench scale experiment

Parameter	OFMSW	Feed
pH	6.12	6.65
TS (%)	19.02	12.30
VS (%)	85.65	85.12
VFA(meq/l)	10.85	10.57
COD(mg/l)	35230	36018
TKN(g/l)	1.04	1.06
TOC(g/l)	22.49	24.5

4.4.1.1 Performance of the Bench Scale Reactor

Digestion during start-up ran for a total of 50 days. Biogas production is the primary indicator to evaluate the performance efficiency of the reactor. Figure 4.24 indicates the daily and cumulative biogas production, where the biogas production was high in the beginning which was due to the entrapped air inside the reactor.

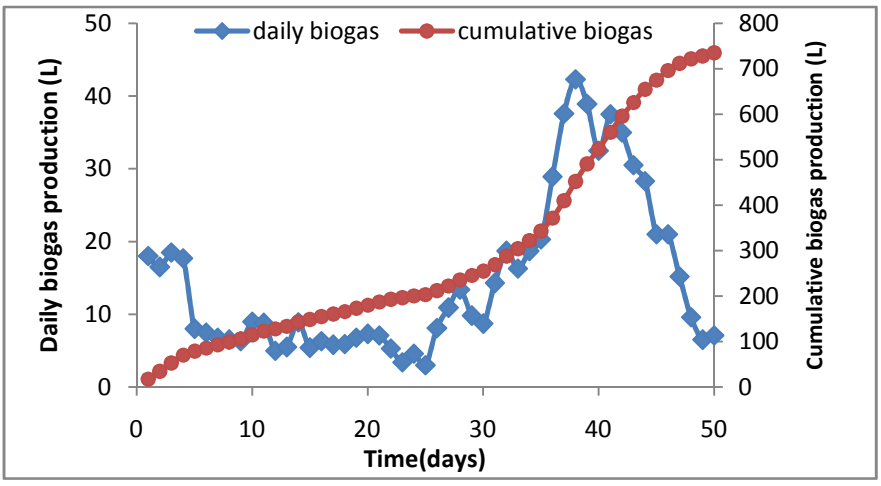


Figure 4.24 Daily and cumulative biogas production during start-up period

From Figure 4.24, it is clear that the biogas production was lower between 5 and 23 days; this may be due to the pH reduction. So after adjusting the pH value in the neutral range by addition of 6N NaOH to the system, the production was increased. pH control favours the biodegradation process (Forster et al., 2008). The highest volume of biogas produced (42.3 L/d) was achieved at day 38. The biogas production rate fell after day 39 indicating exhausting of readily accessible substrate for biogas production. The reactor system was run until the gas production rate peaked and then dropped below 06.5 L of biogas per day. Then, the feeding and withdrawing mode of operation was started. During the start-up phase approximately 735 L biogas was produced.

The pH and VFA variation during the start-up period are shown in Figure 4.25. Initial pH was 6.5, which started to decrease to 6.31. Therefore, small quantities of 6N NaOH were added to the reactor periodically during days 5-24 to maintain pH at near neutral range. It can be noted as small peaks during days 5-24 in Figure 4.25. From day 26 onwards, pH started increasing slowly; therefore, NaOH was not added anymore. It became stable at around 7.8 during days 41-50.

The VFA generation in the beginning was high due to higher acidogenesis and lower methanogenic activity. The initial pH drop and high volatile fatty acid concentration show that the substrate contains some easily biodegradable constituent (Figure 4.25). VFA concentration was increased till 20^{th} day and maximum VFA concentration of 140.5 meq/l was formed on the same day. After that VFA concentration was found decreased due to methanogenic activity in which the intermediate organic acids was started to

convert into biogas. The concentration of VFA dropped from 140.5 meq/l to 42.5 meq/l in 30 days. The reason is that there was no waste feeding throughout the start-up phase.

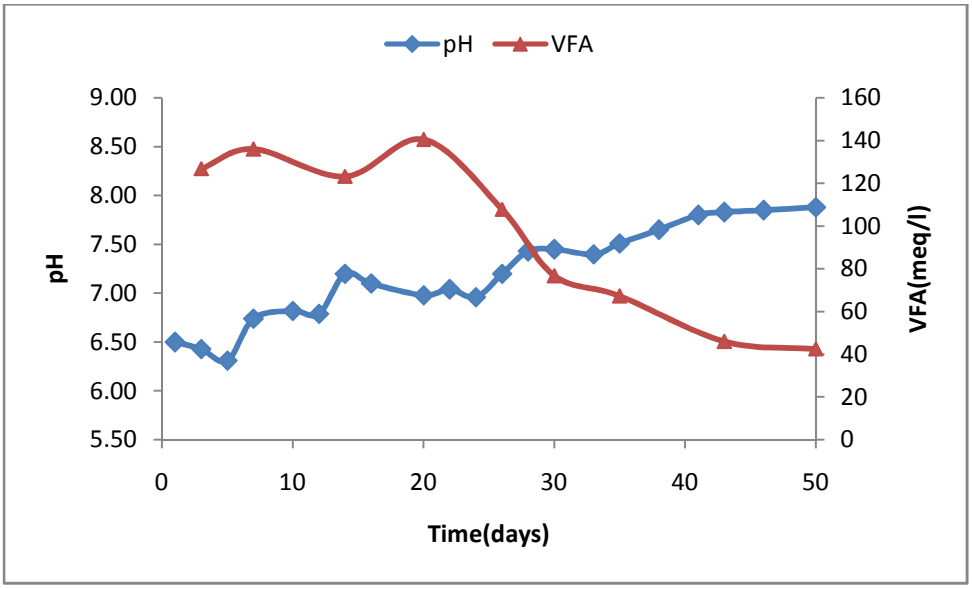


Figure 4.25 Variation of pH and VFA during start-up period

The profile of VFA/Alk ratio during start-up is shown in the Figure 4.26. The evolution of VFA/Alk ratio was different from the VFA concentration. Increase in VFA/Alk ratio after reactor loading was not observed, rather there was a continuous decrease, which indicates that alkalinity started to develop and increase just after loading. After day 20, VFA/Alk ratio started to decrease in the same way as that of VFA. This may be attributed to decrease in VFA concentration.

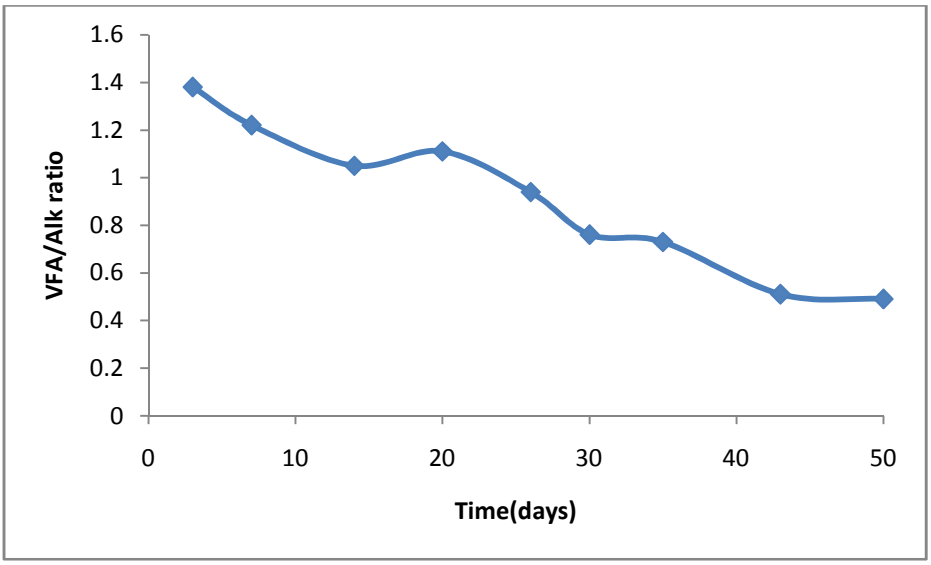


Figure 4.26 Profile of VFA/Alk ratio during start-up

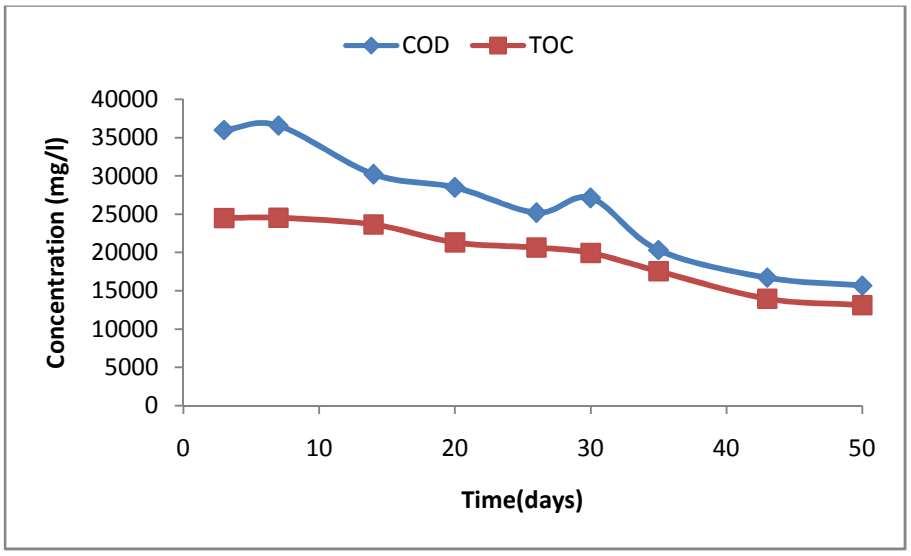


Figure 4.27 Evolution of COD and TOC (mg/l) in the reactor during start up process

The organic content of substrate was measured in terms of chemical oxygen demand and total organic carbon. The Figure 4.27 depicts the variation

of these parameters during start-up process. The significant increase in COD in leachate was observed in the beginning which was the sign of active hydrolyse phase. The COD and TOC of the leachate were found decreasing due to conversion of organic matter into biogas.

Trend of NH_3-N during start-up process is shown in the Figure 4.28. In this experiment, concentration of NH_3-N was increasing due to release of ammonia during hydrolysis of protein or utilisation of nitrogen for biomass synthesis. Ammonia nitrogen is an important parameter for the buffer capacity in an anaerobic reactor. With concentrations of up to 1000 mg/l, ammonia nitrogen stabilizes the pH value. Ammonia nitrogen is released during the anaerobic hydrolysis of protein, causing an increase of the pH value (Fricke et al., 2007).

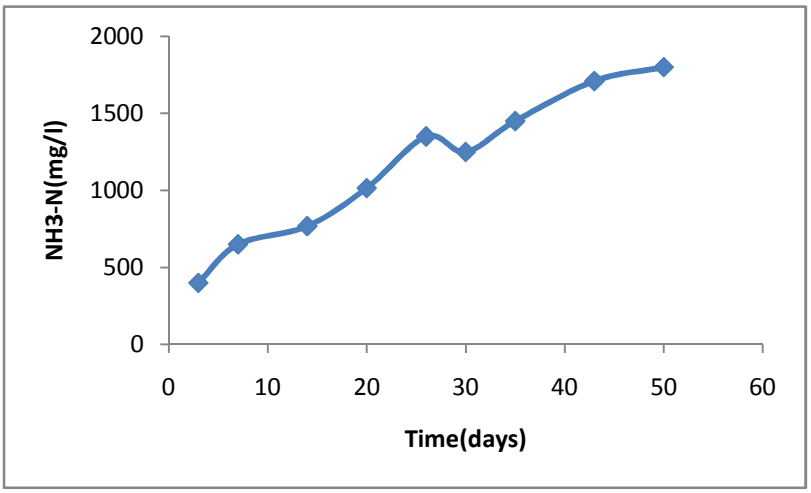


Figure 4.28 Evolution of NH3-N during start up process

It is evident that NH_3-N concentration (>6000 mg/l) indicates the inhibition of methanogens in an acclimated environment (Mata-Alvarez et al., 2000). In this study, the NH_3-N concentration increased from

400 mg/l to 1800 mg/l. So it can be concluded that there is no inhibition of ammonia nitrogen during the AD process of this system.

4.4.2 Continuous Feeding

In this operation, the continuous feeding was applied in draw and feed mode. Experiments were conducted for three different organic loading rates of 3.1, 4.2 and 5.65 kg VS/m^3/d in three consecutive runs (1 to 3) with constant retention time of 30 days.

4.4.2.1 Effect of Organic Loading Rate on Stability Parameters of the Reactor

(i) pH and VFA

In the anaerobic digestion process, methanogenic bacteria is more sensitive to environmental conditions than hydrolytic and acidogenic bacteria. The first criteria was taken into account was pH value. The pH indicates the stability of the system and its variation also depends on the buffering capacity itself (Mata-Alvarez, 2003). The pH is an indicator of good process performance and should be above 7.0 at all times in which case the process operates successfully. With OLR of 3.1 kg VS/m^3/d, the system stabilized its pH at around 7.36 with a range of 7.15-7.6 as shown in Figure 4.29. When the OLR was increased from 3.1 to 4.2 kg VS/m^3/d, pH fell down to 6.8 and regulated to an average of 7.01 (6.8-7.31). As a result of further increase in OLR to 5.65 kg VS/m^3/d, a drastic decrease in pH was observed and pH dropped to the value of 6.5. The decline in pH in the starting days of each of the first two runs and most of the last run is linked to destabilization of the system as a result of increase in OLR. The reason is that when organic loading rate is increased, the acidogens also increase their

activity and produce high amount of VFA, as they are fast growing. But, on the other hand, methanogens owing to their slow specific growth rate cannot utilize all the already produced VFA and need more time to build the required population size. Thus initial and temporary decrease in pH is due to accumulation of VFA as a result of this imbalance in the microbial groups, which is recovered until methanogens build their sufficient population. The decrease of pH is more pronounced while working with higher OLR, i.e., 5.65 kg VS/m^3/d. The reason is that the imbalance between acidogenic and methanogenic activity is more pronounced.

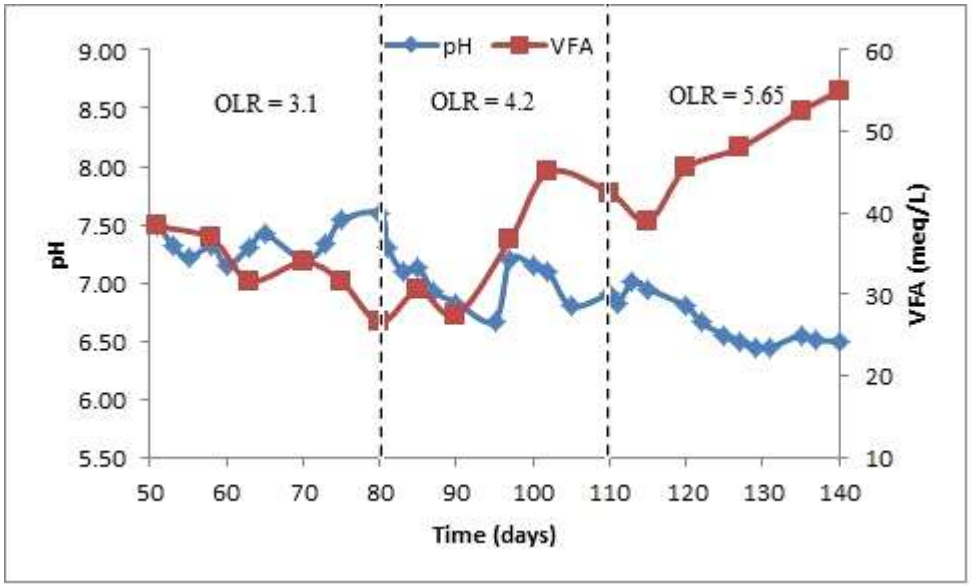


Figure 4.29 Variation of pH and VFA during continuous loading

The concentration of volatile fatty acids in the digestate was quite stable at an average value of 33.2 meq/l (range: 26.6-38.4 meq/l) while operating at OLR of 3.1 kg VS/m^3/d (Figure 4.29). When OLR increased to 4.2 kg VS/m^3/d, the VFA concentration increased and reached a maximum

value of 45 meq/l with an average value of 36.5 meq/l in this run. Finally, at OLR of 5.65 kg VS/m^3/d, the VFA concentration increased to 55 meq/l because the organic loading rate is increased. This trend shows the destabilization of the reactor caused by increase in OLR. It is important to note that at the start of each OLR, the VFA started to accumulate, which is related with imbalance of activity of microbial groups and initial temporary destabilization of reactor as a result of increase in OLR as discussed above in the case of pH. Similarly, at the end of each of first two OLRs, the concentration of VFA declined, which is a sign of stability of the system.

(ii) VFA to Alkalinity ratio (VFA/Alk ratio)

VFA/Alk ratio is a good indicator of digester functioning. With OLR of 3.1 kg VS/m^3/d, this parameter remained between 0.41-0.52 for most of the time (Figure 4.30). This is a good range of VFA/Alk ratio for a working digester. But at OLR 4.2 kg VS/m3/d, the average value of VFA/Alk ratio increased to 0.59, which is still acceptable for an operating digester. However, at OLR of 5.65 kg VS/m^3/d, VFA/Alk ratio increased to very harmful range (0.72-0.83), because at VFA/Alk ratio of 0.8, significant pH reduction and digester failure happen (Khanal, 2008).The trend of VFA/Alk ratio almost followed the trend of VFA concentration, except at the day 63, where VFA concentration decreased but VFA/Alk ratio did not follow it, because the system had low buffering capacity or alkalinity. Hence, rise in VFA concentration did not show any adverse effect on this ratio and hence system performance.

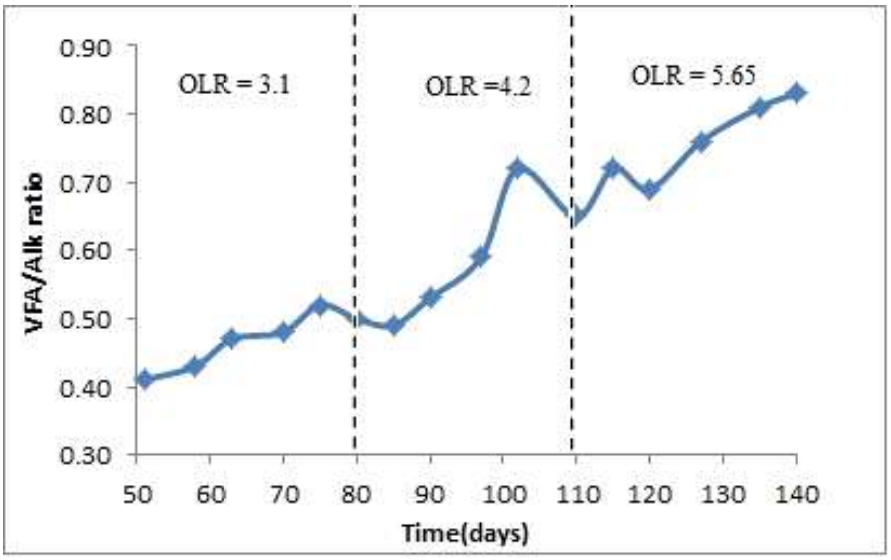


Figure 4.30 VFA/Alk ratio in the digester during continuous loading

(iii) COD and TOC

Figure 4.31 presents the variation of COD and TOC concentrations in leachate. During run 1 (OLR-3.1 kg VS/m^3/d), these concentrations were found significantly decreased after the completion of the retention time. But COD and TOC in leachate were found at the higher concentrations in loading rate 2 (OLR-4.2 kg VS/m^3/d) and 3(OLR-5.65 kg VS/m^3/d) during the digestion. This can be explained that there was higher hydrolysis but less methanogenesis because hydrolytic bacteria are more robust to environmental condition. As the organic loading rate is increased, the COD degradation decreased.

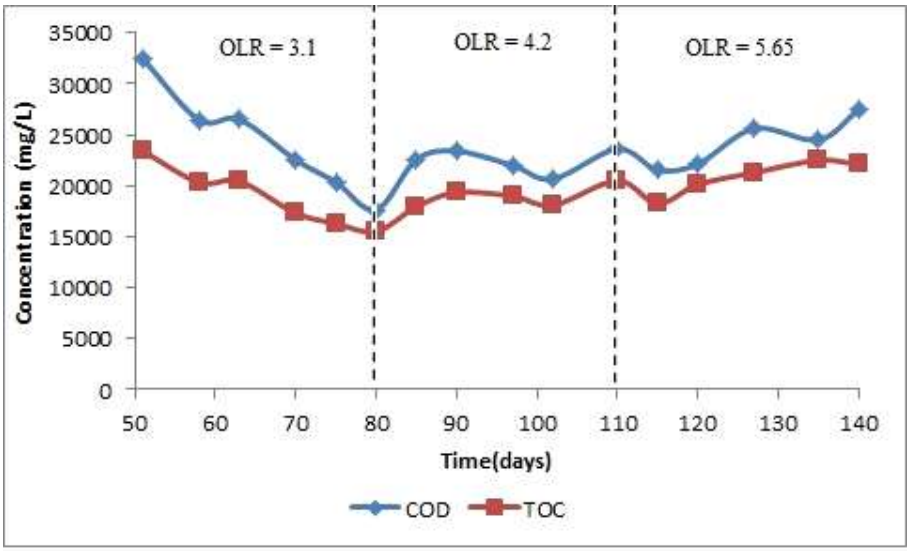


Figure 4.31 Variations of COD and TOC during continuous operation

(iv) Ammonia nitrogen (NH_3-N)

The presence of ammonia nitrogen can always be of concern in anaerobic digestion as free ammonia can be inhibitory. Ammonia is the end product of anaerobic degradation of proteinase materials. Protein first converted into amino acid in hydrolysis stage, and then further degraded anaerobically in acidification stage producing ammonia. The Variation of NH_3-N during continuous feeding is shown in the Figure 4.32. In this experiment, concentration of NH_3-N was high during run 1, with an average value of 1933 mg/l. But these concentrations were lower in runs 2 and 3 due to falling of pH value and less degradation of proteinase materials. At the OLRs of 4.2 and 5.65 kg VS/m^3/d, the average values of NH_3-N were 1806 mg/l and 1784 mg/l respectively. The inhibition concentration of ammonia nitrogen as reported by Mata- Alvarez, 2000 is 6000 mg/l which is higher than the ammonia concentration obtained in this experiment. So it can be

concluded that there was no inhibition of ammonia nitrogen during the AD process of this system.

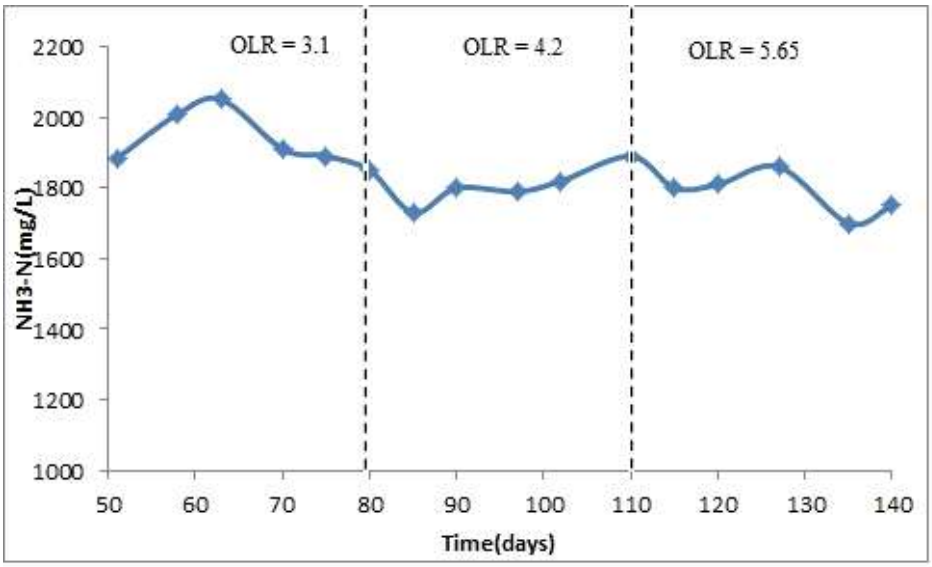


Figure 4.32 Variation of NH3-N during continuous feeding

4.4.2.2 Performance of Bench Scale Reactor at Different Loading Rate

(i) Biogas production

Biogas production was monitored daily. One of the main objectives of this research was to determine the performance of the AD process when operated at different loading rates. For the purpose of evaluating this system on the effect of loading rate, biogas production, specific biogas production or biogas yield and VS reduction were taken into account as the indicators to assess the reactor performance of each loading rate. The daily and cumulative biogas productions during continuous loading are shown in Figure 4.33. Biogas production rate during the loading rates 3.1,4.2 and 5.65 kg VS/m^3/d were approximately with an average value of 34 L/d, 28 L/d and

21.6 L/d respectively. It can be noted that at the end of OLR 3.1 and 4.2 kg VS/m^3/d, the gas production rate becomes stable. This is related with stable pH and VFA concentration of the system at the mentioned time. The decrease in biogas production rate was almost linear with increase in OLR during first two runs. But, during run 3 (i.e. OLR 5.65 kg VS/m^3/d), the gas production rate did not decrease with the same rate as that of OLR. This could be explained by drastic increase in VFA/Alk ratio (or drop in alkalinity) during that run.

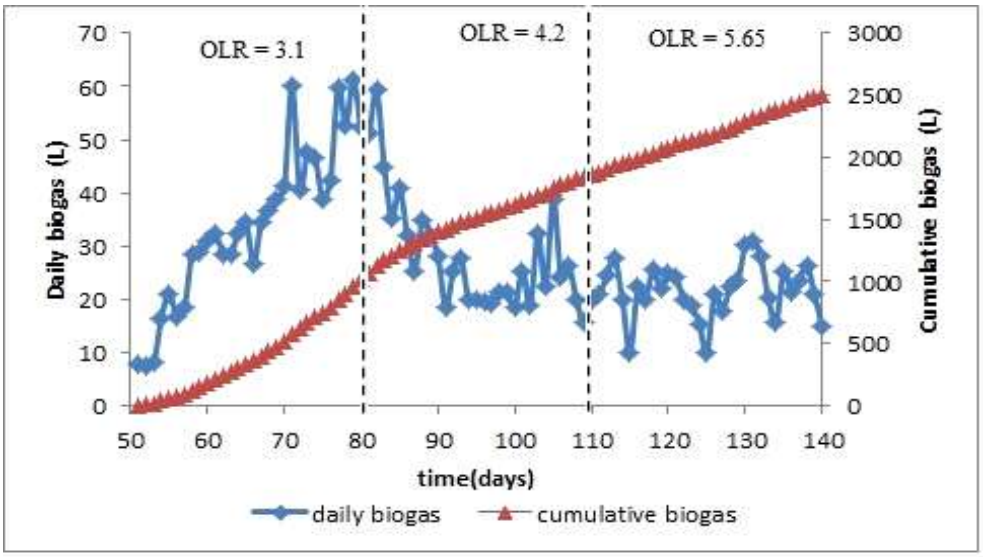


Figure 4.33 Daily and cumulative biogas production during different OLRs

(ii) VS removal and Specific biogas production

Volatile solid reduction is taken into account to evaluate the reactor performance and stability of the digestaste. The characteristics of feed and digestate during continuous loading at different loading rates are given in the Table 4.10. VS degradation value of 65.9 % was achieved when operating at OLR 3.1 kg VS/m^3/d. On the other hand, while the runs 2 and 3

with increased OLR of 4.2 and 5.65 kg VS/m^3/d, VS degradation values were 55.2 % and 43.7 % respectively as illustrated in Figure 4.34. Comparably, these VS reduction is lower with result found by Castillo et al. (2006) who reported that VS reduction of 77.1% was obtained with the digestion time of 25 days. This lower value may be due to the reactor configuration. But, these results are similar to those obtained by Gallert and Winter, (1997). They obtained VS removal of 65 % in a thermophilic system operating at OLR of 9.5 kg VS/m^3/d and 18% TS.

Table 4.10 Characteristics of feed and digestate during continuous loading

Run	Feed		Digestate		VS reduction (%)
	TS (%)	VS (%)	TS (%)	VS (%)	
1	12.92	84.20	7.2	51.47	65.9
2	11.53	81.60	6.94	60.62	55.2
3	13.21	83.87	8.92	69.85	43.7

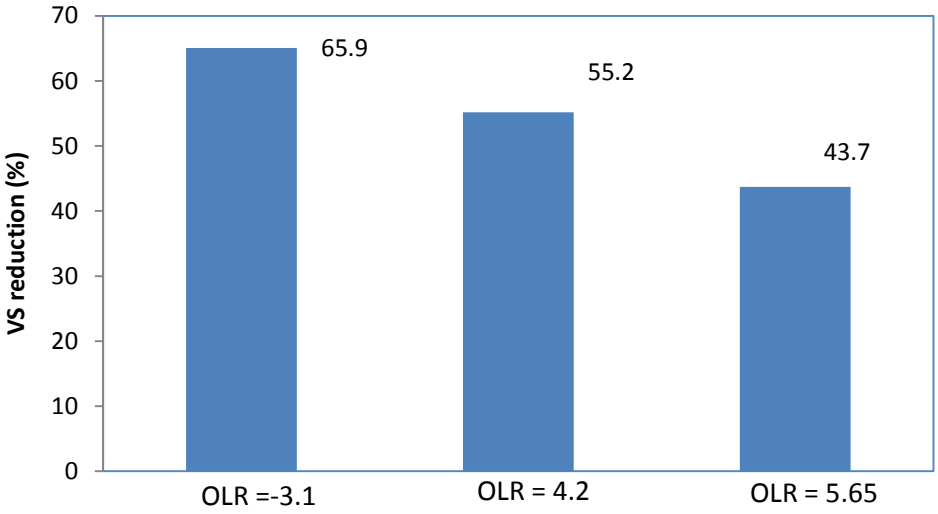


Figure 4.34 Volatile solid degradation for various loading rates

Figure 4.35 presents the specific biogas production or biogas yields for various loading rates. The highest specific biogas production observed is 368 L/kg VS at OLR of 3.1 kg VS/m^3/d. As the loading rate was increased, a decreases in the biogas yields (229 L/kg VS and 130 L/kg VS) are observed at OLR of 4.2 kg VS/m^3/d and 5.65 kg VS/m^3/d respectively. The overloading is marked by the fall in pH and gas yield. However, the specific biogas production of 368 L/kg VS fed at OLR of 3.1 kg VS/m^3/d of this study is in line with the biogas yield values found in literature.

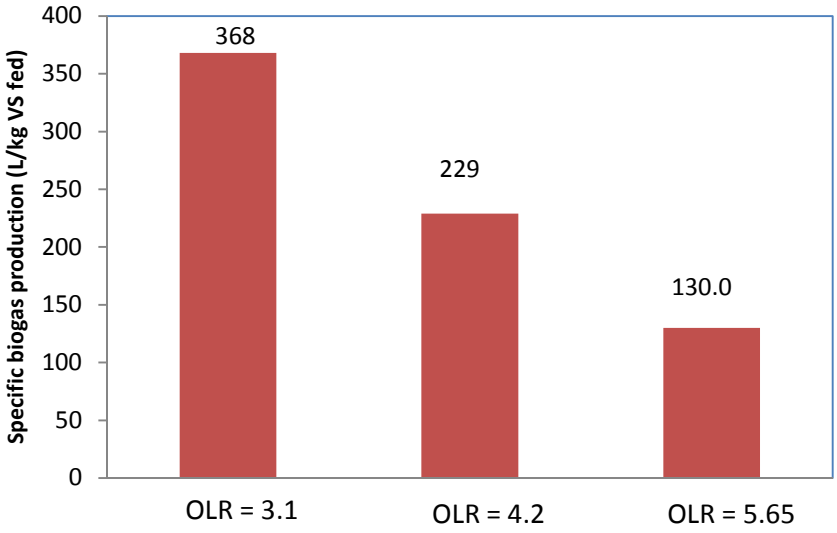


Figure 4.35 Profile of specific methane production for various loading rates

The biogas yield reported by various authors through dry anaerobic digestion of OFMSW at thermophilic conditions is in the range of 350-500 L /kg VS added (Gallert and Winter, 1997; Pavan et al., 2000; Montero et al., 2008; Bolzonella et al., 2003). Similarly, biogas yield reported for WS-OFMSW under mesophilic semi- dry anaerobic digestion is 423L/kg VS added (L. Dong et al., 2010). It should be cautioned here that the optimum

loading rate of 3.1 kg VS/m^3/d observed here is not universal as the optimal rate depends upon the reactor configuration (Pavan et al. 2000).

4.4.3 Digestate Quality

Apart from biogas, the AD process also produces solid and liquid byproducts (digestate). The quantity, quality and nature of these products depend upon the quality of the feedstock to the AD process and the method of digestion. Literature shows the digestate have certain amount of plant nutrients and organic matter and can be used as organic fertilizer or soil conditioner. Digestate was removed from the reactor every day before feeding of fresh waste throughout the reactor operation period. The liquid (leachate) is separated from the freshly withdrawn digestate through a strainer. The residue (solid digestate) was analysed for moisture, TS and VS content once in a week. Moreover, digestate was also characterised for carbon and nitrogen content to calculate its C/N ratio. Table 4.10 shows the quality of digestate.

Table 4.11 Quality of the digestate

Run	Feed		Digestate		Digestate (C/N)
	TS (%)	VS (%)	TS (%)	VS (%)	
1	12.92	84.20	7.2	51.47	14.5
2	11.53	81.60	6.94	60.62	12.8
3	13.21	83.87	8.92	69.85	13.6

Total solids content of digestate ranged from 7-9% during continuous loading. Thus there was no significant difference in the digestate solid content among different runs of this experiment. Based on the property of digestate (i.e. C/N ratio 12-15), further intensive treatment, for instance,

composting, is not required. The digestate can be directly applied to agricultural fields. Wood (2008) also stated that C/N ratio of organic material fit for agricultural land application should be < 20.

4.4.4 Conclusions

The bench scale study of the semi-continuous AD process revealed that start-up of the mesophilic anaerobic digestion of OFMSW is effective. During the continuous operation, when the loading rate was increased, the biogas production was decreased. Specific biogas production or biogas yield dropped from 368 L/kg VS to 130 L/kg VS, when loading rates increased from 3.1 kg VS/m^3/d to 5.65 kg VS/m^3/d. The highest VS degradation of 65.9% was obtained with OLR of 3.1 kg VS/m^3/d at a retention time of 30 days. From the present study the optimum loading rate obtained for maximum biogas production was 3.1 kg VS/m^3/d.

Chapter 5

MATHEMATICAL MODELLING AND SIMULATION

Contents

5.1 Introduction

Mathematical modelling and simulation serve to analyse processes in a complex system such as AD and to simulate specific operational situations. Over the last three decades, many different anaerobic models have been developed, however their use was often limited due to their specific nature (Gavala et al. 2003). Based on the wide variety of anaerobic models available, the International Water Association (IWA) Task Group for Mathematical Modelling developed one model, namely the Anaerobic Digestion Model No 1 (ADM1) (Batstone et al. 2002a). Trying to serve as a generic platform, ADM involves a total of 19 biochemical processes with seven species utilizing eight intermediates, as well as three sorts of physiochemical processes. As benefits, the Task Group expects the following (Batstone et al. 2002b):

- Increased model application for full-scale plant design, operation and optimization
- Further development work on process optimization and control, aimed at direct implementation in full-scale plants
- Common basis for further model development and validation studies to make outcomes more comparable and compatible
- Assisting technology transfer from research to industry

Many authors have, since the release of the ADM1 model, showed that it possesses good predictive capabilities for different configurations of anaerobic digestion processes (Wayne and Parker 2005; Blumensaat and Keller 2005). Papers using anaerobic digestion with the ADM1 model when co-digesting food waste with another substrate note that the model, at the very least, predicts the average trend of transient (variation with time) processes (Derbal et al, 2009). Predictions for volatile fatty acids in the digester can be over predicted in steady state systems with small reactors and high volumetric flows if the default model is used, i.e. a model not adapted in any way to a specific waste (Wayne and Parker, 2005). The purpose of the present chapter is to develop a model by adapting default ADM1 model in order to predict the performance of a mesophilic continuous anaerobic digester for the treatment of OFMSW at different OLRs. The proposed model is based on the cited ADM1 model (Batstone et al., 2002b). In the following section gives complete description of ADM1 model, adapted ADM1 model, implementation of adapted ADM1 model in MATLAB® and simulation of continuous digester.

5.2 The Anaerobic Digestion Model No. 1 (ADM1)

The ADM1 model is one of the most comprehensive AD models and thus model complexity in terms of number of differential equations and parameters is high. Most composition and process variables are expressed in COD concentrations (kg COD/m³) except nitrogen (NH_4^+ and NH_3) and inorganic carbon (CO_2 and HCO_3^-) concentration variables which are expressed in kmol N/m³ and kmol C/m³ respectively. In general, the process of anaerobic digestion can be divided into biochemical and physico-chemical processes. Biochemical processes describe intracellular processes such as the degradation of soluble organic material by different bacterial populations resulting in biomass growth and decay, and extracellular processes such as disintegration of particulate organic material and enzymatic hydrolysis. Physico-chemical processes include ion association and dissociation and liquid-gas transfer. Both processes are needed for comprehensive modelling of AD processes as physicochemical state variables such as pH, carbon buffer and biogas composition strongly affect the biochemical reactions causing inhibitions and thus a rate-limiting effect.

The state of the ADM1 is described by 24 variables that can be divided into two main groups of soluble and particulate components, which are labelled as S and X respectively. These two groups are subsequently split into inert components expressed by S_I and X_I and further degradable components. Those degradable soluble components consist of organic and inorganic compounds whereas the particulate components apart from X_I are considered to be organic as the inorganic compounds are part of X_I. A list of all soluble as well as particulate state variables of the ADM1 and their corresponding notation is shown in Table 5.1.

Table 5.1 ADM1 state variables

Monosaccharaides (kg COD /m^3)	S_{su}
Amino acids (kg COD /m^3)	S_{aa}
Long chain fatty acids (kg COD /m^3)	S_{fa}
Total valerate (kg COD /m^3)	S_{va}
Total butyrate (kg COD /m^3)	S_{bu}
Total propionate (kg COD /m^3)	S_{pro}
Total acetate (kg COD /m^3)	S_{ac}
Hydrogen gas (kg COD /m^3)	S_{h2}
Methane gas (kg COD /m^3)	S_{ch4}
Inorganic Carbon (k mole C/ m^3)	S_{co2}
Inorganic Nitrogen (k mole N/ m^3)	S_{nh4}
Soluble inerts (kg COD/ m^3)	S_I
Composites (kg COD/ m^3)	X_c
Carbohydrates (kg COD/ m^3)	X_{ch}
Proteins (kg COD/ m^3)	X_{pr}
Lipids (kg COD/ m^3)	X_{li}
Sugar degraders (kg COD/ m^3)	X_{su}
Amino acid degraders (kg COD/ m^3)	X_{aa}
LCFA degraders (kg COD/ m^3)	X_{fa}
Valerate and butyrate degraders (kg COD/ m^3)	X_{c4}
Propionate degraders (kg COD/ m^3)	X_{pro}
Acetate degraders (kg COD/ m^3)	X_{ac}
Hydrogen degraders (kg COD/ m^3)	X_{h2}
Particulate inerts (kg COD/ m^3)	I

The COD mass flow through the biochemical processes for a composite particulate material as implemented in ADM1 is shown in Figure 5.1. It becomes clear that it is of most importance for the accuracy of the model to well define the input characteristics in terms of COD. Defining the biodegradable input COD is necessary, as a considerable fraction of the

input COD may be anaerobically not degradable. Secondly, the determination of dissolved and particulate COD is recommended as it has a significant impact on the COD mass flow. It is thirdly recommended to determine the composition of carbohydrates, proteins and lipids in the composite particulate material. In a first step the complex source substrate is split into an inert and a degradable COD fraction, where the degradable fraction disintegrates to carbohydrates, proteins and lipids. The compounds are then degraded to sugars, amino acids and LCFA before they are transformed into organic acids and hydrogen, which are eventually used to produce methane.

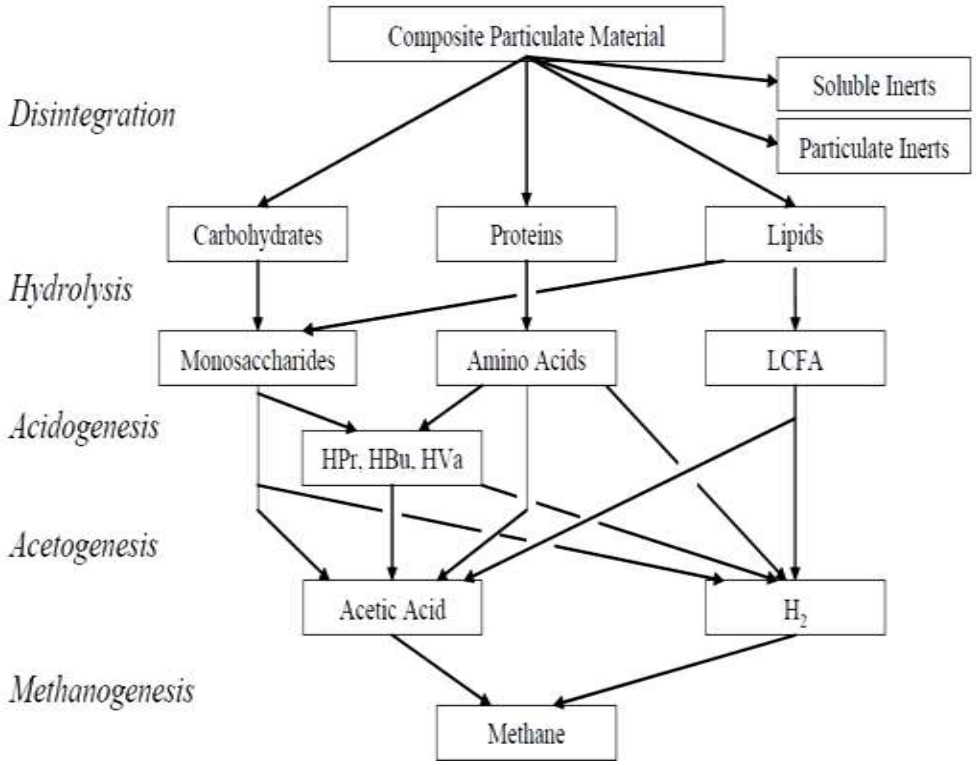


Figure 5.1 COD mass flow for a particulate composite as used for ADM1. Propionic acid (HPr), Butyric acid (HBu) and Valeric acid (HVa) are grouped in the figure for simplicity ***(Source:*** **Batstone et al. 2002b***).*

The structure of ADM1 is formulated by a Peterson Matrix. This matrix was developed by Peterson (1965) to construct chemical and biological models in a flexible way. In the matrix, each row represents one process and each column represents one component. The reaction rates of processes are displayed on the right side of the matrix, where the coefficients between processes and components are distributed inside the matrix. The ADM1 matrix of biochemical processes are given in Annexure III. More explanation of these matrixes is narrated in following sections.

5.2.1 Biochemical Processes

There are five main biochemical processes happening during anaerobic digestion, specifically disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis. These processes are catalysed by a vast number of different microorganisms present in the microbial community of an anaerobic digester. These microorganisms are grouped according to their main substrate, for example sugar degraders, Xsu and acetate degraders Xac. The activity of the different microorganisms is generalised per group and represented by a simplified kinetic equation. The summary of the process and corresponding rate equations of the ADM1 is given in the Table 5.2.

Table 5.2 Summary of the process rate equations of the ADM1.

j	Process	Rate, ρ_j [kg COD /m^3/d]
1	Disintegration	$k_{dis} X_c$
2	Hydrolysis of Carbohydrates	$k_{hyd,ch} X_{ch}$
3	Hydrolysis of Proteins	$k_{hyd,pr} X_{pr}$
4	Hydrolysis of Lipids	$k_{hyd,li} X_{li}$
5	Uptake of Sugars	$k_{m,su} \frac{S_{su}}{K_s + S_{su}} X_{su} I_1$
6	Uptake of Amino Acids	$k_{m,aa} \frac{S_{aa}}{K_S + S_{aa}} X_{aa} I_1$
7	Uptake of LCFA	$k_{m,fa} \frac{S_{fa}}{K_S + S_{fa}} X_{fa} I_2$
8	Uptake of Valerate	$k_{m,c4} \frac{S_{va}}{K_S + S_{va}} X_{c4} \frac{I}{1 + S_{bu}/S_{va}} I_2$
9	Uptake of Butyrate	$k_{m,c4} \frac{S_{bu}}{K_S + S_{bu}} X_{c4} \frac{I}{1 + S_{va}/S_{bu}} I_2$
10	Uptake of Propionate	$k_{m,pro} \frac{S_{pro}}{K_S + S_{pro}} X_{pro} I_2$
11	Uptake of Acetate	$k_{m,ac} \frac{S_{ac}}{K_S + S_{ac}} X_{ac} I_3$
12	Uptake of Hydrogen	$k_{m,h2} \frac{S_{h2}}{K_S + S_{h2}} X_{h2} I_1$
13	Decay of X_{su}	$k_{dec,X_{su}} X_{su}$
14	Decay of X_{aa}	$k_{dec,X_{sa}} X_{aa}$
15	Decay of X_{fa}	$k_{dec,X_{fa}} X_{fa}$
16	Decay of X_{c4}	$k_{dec,X_{c4}} X_{c4}$
17	Decay of X_{pro}	$k_{dec,X_{pro}} X_{pro}$
18	Decay of X_{ac}	$k_{dec,X_{ac}} X_{ac}$
19	Decay of X_{h2}	$k_{dec,X_{h2}} X_{h2}$

Disintegration and hydrolysis

Disintegration and hydrolysis are biochemical extracellular processes that create consumable substrates from dead cells and solid feed. Composite particles fall apart in lipid, carbohydrate and protein particles. These particles are hydrolysed into fatty acids, sugars and amino acids respectively. These extracellular reactions are mostly dependent on the surface area of the substrate, as it is assumed that extracellular enzymes are produced by organisms growing on the particle surface. This is best represented by first-order kinetics as we are assuming that the rate of disintegration or hydrolysis is proportional to the substrate concentration. The common expression of first-order kinetics is shown as follows:

$$\rho_i = k_i X_i \quad \text{.....(5.1)}$$

Where, ρ_i = uptake rate of substrate i (kg COD/m^3/d)

ki = parameter of first order kinetics of particulate component i (1/d)

Xi = particulate component i (kg COD/m^3)

The parameter k_{dis} is used for disintegration, where the parameters $k_{hyd,ch}$, $k_{hyd,pr}$ and $k_{hyd,li}$ are used for the hydrolysis of carbohydrates (ch), proteins (pr) and lipids (li), respectively.

Substrates uptake

Following hydrolysis, three steps acidogenesis, acetogenesis and methanogenesis are intracellular process. They are used to describe the utilisation of substrates by microorganisms. Seven species are involved in three steps, namely sugar degraders, amino acids degraders, LCFA degraders, valerate and butyrate degraders, propionate degraders, acetate degraders and hydrogen degraders.

For substrate uptake Monod-type kinetics are used as the basis for all intracellular biochemical reactions (Haridas et al., 2005). Biomass growth is implicit in substrate uptake.

$$\rho = k_m \cdot \frac{S}{K_s + S} \cdot X \cdot I_1 \cdot I_2 \cdot I_n \cdots \quad \text{.....(5.2)}$$

Where:

ρ = substrate uptake rate (kg COD/ m^3/ d),

k_m = maximum specific uptake rate (1/d),

S = substrate concentration (kg COD/ m^3),

K_S = half-saturation coefficient (kg COD/ m^3),

X = substrate-specific biomass (particulate) concentration (kg COD/ m^3),

$I_1 ... I_n$ = modifiers included to describe inhibition

Death of biomass

The decay of biomass is the indispensable step of the biochemical processes. Death of biomass is represented by first order kinetics, and dead biomass is maintained in the system as composite particulate material.

Inhibition

Anaerobic digestion processes are very sensitive and fragile biological processes. Improper surroundings or changes can destroy the anaerobic digestion process totally. Hence, it is essential to include the inhibition function in the model (Feng, Y, 2004). The inhibition factor is implemented in ADM1 by timing inhibition term with substrate uptake rate.

All the uptake processes are sensitive to one or more inhibitors. Inhibition functions considered in ADM1 include pH (all groups), hydrogen

(acetogenic groups) and free ammonia (aceticlastic methanogens). pH inhibition is implemented as one of two empirical equations, while hydrogen and free ammonia inhibition are represented by non-competitive functions. The other uptake-regulating functions are secondary Monod kinetics for inorganic nitrogen (ammonia and ammonium), to prevent growth when nitrogen is limited, and competitive uptake of butyrate and valerate by the single group that utilises these two organic acids (Batstone et al., 2002b).

pH inhibition is described by an empirical relation shown in eq. (5.3). The pH limits border the transitional area between completely inhibited and completely uninhibited.

$$I_{pH} = e^{-3\left(\frac{pH - pH_{UL}}{pH_{UL} - pH_{LL}}\right)^2} \quad \text{.....(5.3)}$$

In all uptake reactions nitrogen is also taken up to create biomass. When there is a low nitrogen concentration, uptake processes will be slower. This secondary substrate inhibition is modelled by eq. (5.4). Constant K_S is the nitrogen concentration where inhibition is 50%.

$$I_{iN,\lim} = \frac{1}{1 + K_s / S_{iN}} \quad \text{.....(5.4)}$$

Ammonia inhibits aceticlastic methanogenesis and hydrogen inhibits acidogenesis and acetogenesis. It is assumed both inhibitions can be modelled by competitive inhibition (eqs. 5.5 & 5.6). Constant K_I is the inhibitor concentration where the inhibition is 50%.

$$I_{nh3} = \frac{1}{1 + \frac{S_{I\,nh3}}{K_{I\,nh3}}} \quad \text{.....(5.5)}$$

$$I_{h2} = \frac{1}{1 + \frac{S_{h2}}{K_{I\,h2}}} \quad \text{.....(5.6)}$$

5.2.2 Physico-chemical Processes

AD is sensitive to physical conditions; therefore physico-chemical processes are integrated into the model. In ADM1, two major types of physico-chemical reactions are implemented.

a) Liquid-liquid processes (mainly acid-base reactions).
b) Liquid-gas processes (liquid-gas transfer of the biogas compounds).

Liquid-liquid processes are characterized by ion association and dissociation with hydrogen and hydroxide ions. These are called the acid-base-reactions. ADM1 proposes two different possibilities to integrate the acid-base-reactions into the model, as they are so rapid, they can firstly be referred to as equilibrium process. Secondly, they can be described as dynamic process with high kinetic coefficients. Feng et al., (2004) studied both approaches for the relevant processes which are NH_4^+/NH_3, CO_2/HCO_3 and HCO_3/CO_3^{2-}. He found that the differences between the approaches are so small that they can be ignored. Thus, the ADM1 recommendation to use the equilibrium approach is followed in this work.

Liquid-gas processes are most important in the model as the production of biogas is one of the benefits of AD. The biogas contains CH_4, CO_2, and water vapour, as well as some other trace gases like N_2 and H_2S.

Because of their strong impact on biological processed or outputs, CH_4, CO_2 and H_2 are considered in ADM1 (Batstone et al., 2002b). N_2 is not included as its solubility is so high that the mass flow to gas is negligible compared to that in the output. H_2S is not included because sulphate reduction is not included either in the model. The liquid-gas processes for these three components are implemented by Henry's law. The physico-chemical processes are implemented according to ADM1 and the modified model by Feng (2004).

5.3 Adapted ADM1

Anaerobic Digestion Model No 1(ADM1) can be adapted to different applications by adjusting the many parameters, including reaction kinetics and substrate composition. The default ADM1 is adapted for modelling the anaerobic digestion of OFMSW. In the original ADM1 model, methane production is temperature dependent with either mesophilic conditions or thermophilic conditions, but the proposed model is developed for mesophilic condition only. In this modelling we assume that the ingoing protein, lipids and carbohydrate fractions are readily available for the biomass. The proposed model has 34 dynamic state variables, considers both biochemical and physicochemical processes and contains several inhibition factors including 3 gas components. The number of processes considered is 28.

5.3.1 Characterisation of OFMSW

In the section 5.1, it was explained that the ADM1 model takes "input" values in terms of COD. However, COD measurements on solid heterogeneous substrates, such as OFMSW, are according to one of the

ADM1 authors "always difficult and open to some uncertainty" (Angelidaki et al., 2009). The data for waste are given terms of VS content. VS content directly relates to another common measurement for solid substrates, namely total solids (TS). It is therefore necessary to convert measurements in VS to COD to be used in ADM1 simulations. A method for doing this is described by Angelidaki and Sanders (2004), using the stoichiometric relationships between completely oxidized waste molecules and the oxygen necessary for complete oxidation.

A biological compound composed of carbon, hydrogen and oxygen is fully oxidized and converted to carbon dioxide and water. The biological compound is composed of 'n' carbon atoms, 'a' hydrogen atoms and 'b' oxygen atoms. Using eq. (5.7) fractions of carbon dioxide and water can be determined. And the ratio between VS and COD can be defined by eq. (5.8).

$$C_nH_aO_b + \left(n + \frac{a}{4} - \frac{b}{2}\right)O_2 \rightarrow nCO_2 + \frac{a}{2}(H_2O) \quad \text{.....(5.7)}$$

$$\frac{COD}{VS} = \frac{\left(n + \frac{a}{4} - \frac{b}{2}\right) * 32}{12n + a + 16b} \quad \text{.....(5.8)}$$

If the VS content and molecular formula is known, the COD can be calculated using eq.(5.8). The constants 32, 12, 16 represent the molar mass of one oxygen molecule (O_2), one carbon atom (C) and one oxygen atom (O) respectively. It is possible to use an extended form of equation (5.7), to include nitrogen, but one must assume in which form nitrogen is oxidized. Angelidaki and Sanders (2004) state that nitrogen (N) should preferably stay in a reduced form. If so, the COD/VS ratio for any waste that also contains

nitrogen can be calculated using equations (5.9) and (5.10) (Angelidaki and Sanders, 2004).

$$C_nH_aO_bN_c + xO_2 \rightarrow yCO_2 + zH_2O + vNH_3 \quad \text{.....(5.9)}$$

$$\frac{COD}{VS} = \frac{32x}{12n + a + 16b + 14c} \quad \text{.....(5.10)}$$

COD/VS fractions for proteins, lipids and carbohydrate are shown in table 5.3.

Table 5.3 Assumed substrate composition and COD/VS fractions (Source: Angelidaki and Sanders,2004).

Substrate type	Composition	COD/VS conversion factor (kg/kg)
Carbohydrate	$(C_6H_{10}O_5)_n$	1.19
Protein	$C_5H_7NO_2$	1.42
Lipids	$C_{57}H_{104}O_6$	2.90

Food waste is mainly composed of protein, lipids and carbohydrates (Zaman 2010; Jansen et al, 2004). The distribution ratio among inert, carbohydrates, proteins, lipids and volatile fatty acids were assumed based on data from literature. The distributions of COD in OFMSW are given in Table 5.4.

Table 5.4 Distribution of COD in OFMSW

Particulate COD (72%)				
Degradable (90%)			Inert (10%)	
Carbohydrates (68 %)	Proteins (18 %)	Lipids (14%)	Soluble (50%)	Particulate (50%)
Dissolved COD (28%)				
Acetic acid (71%)	Propionic acid (18 %)	Butyric acid (7 %)	Valeric acid (4%)	

5.3.2 Mass Transfer Rate Processes

The reactor implemented in the proposed model is assumed as a single-stage CSTR. The model is based on mass balances as visualized in Figure 5.2. In this model, besides all necessary parameters and variables, as well as processes (both biochemical and physicochemical processes), the model further contains two compartments, i.e. the reactor and the headspace, which represent the liquid phase and headspace, separately.

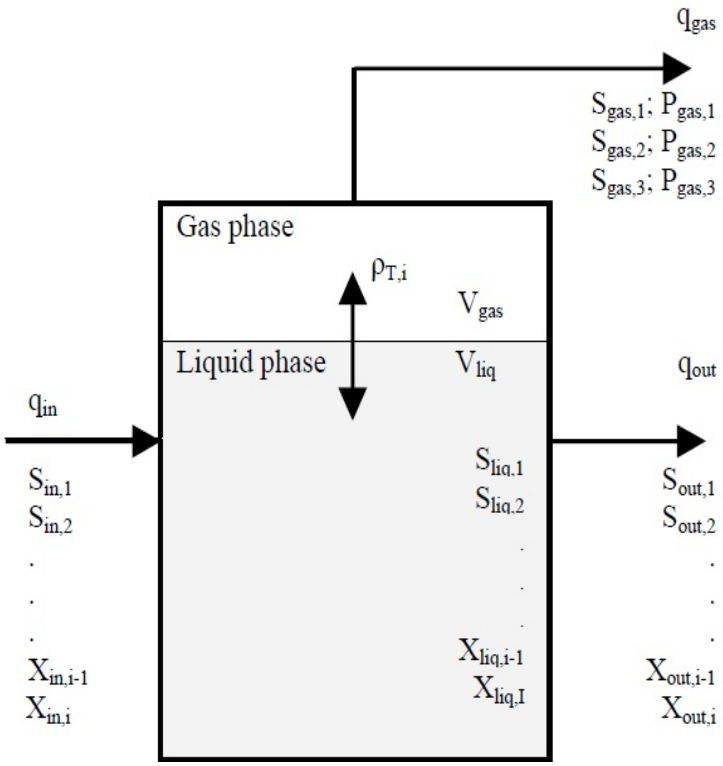


Figure 5.2 Scheme of a single-tank digester (*Source*: Batstone et al., 2002a)

Equations in the liquid phase

According as the mass balance, the state of each component in liquid phase can be expressed as follows:

$$\frac{dS_{liq,i}}{dt} = \frac{q_{in}S_{in,i}}{V_{liq}} - \frac{q_{out}S_{liq,i}}{V_{liq}} + \sum_{j=1-19}\rho_j \nu_{i,j} \quad \text{.....(5.11)}$$

Where,

ρ_j is the reaction rate of process j and $v_{i,j}$ is the stoichiometric coefficients.

S_i is the component concentration (kg COD/m^3), q is the flow (m^3 /day) and V_{liq} is the volume of the reactor (m^3).

If the reactor is fed discontinuously and the liquid phase volume is constant, so during the non-feeding period (batch process), the equation 5.11 can be simplified as:

$$\frac{dS_{liq,i}}{dt} = \sum_{j=1-19}\rho_j \nu_{i,j} \quad \text{.....(5.12)}$$

Equations in the gas phase

In the gas phase, the three main gases CH_4, H_2 and CO_2 present in biogas are dealt with.

Likewise, the following equation can be obtained based on the mass balance:

$$\frac{dS_{gas,i}}{dt} = -\frac{q_{gas}S_{gas,i}}{V_{gas}} + \rho_{T,i}\frac{V_{liq}}{V_{gas}} \quad \text{.....(5.13)}$$

Where, V_{liq} is the liquid volume of the anaerobic reactor, V_{gas} is the gas volume of the anaerobic digester. $S_{gas,i}$ is the concentration of gas number i.

The transfer of gas between the liquid and the gas phase mainly depends on the gas concentration in the liquid phase ($S_{liq,i}$) and the corresponding partial pressure of the gas phase ($P_{gas,i}$). Based on Henry's law a steady state is achieved between both phases. Based on these, the gas transfer rates can be presented in the following equation.

$$\rho_{T,i} = k_L a.(S_{liq,i} - K_{H,i} P_{gas,i}) \quad \text{.....(5.14)}$$

Where ,

$\rho_{T,i}$ = specific mass transfer rate of gas i,
(kg COD/m^3/d for CH_4 and H_2; mole C/m^3/d for CO_2)

K_La = overall mass transfer coefficient K_L times the specific transferarea a (1/d)

$S_{liq.i}$ = concentration of gas i in liquid phase, (g COD/m^3 for CH_4 and H_2; mole C/m^3 for CO_2)

$P_{gas,i}$ = partial pressure of gas i in gas phase (bar)

$K_{H,i}$ = Henry's law coefficient of gas i (mole/m^3/bar)

The partial pressure of each gas is necessary and can be calculated by ideal gas law:

$$P_{gas,i} = S_{gas,i} \cdot R \cdot T \quad \text{.....(5.15)}$$

Due to the fact that gas concentrations in the ADM1 are modelled by COD-based state variables the Henry constant KH needs to be corrected by a factor 16 and 64 for H_2 and CO_2 respectively in order to convert kg COD to k mole.

The gas flow from the created gas in the digester was assumed to be channelled through an orifice and eqn (5.12) was used to calculate gas flow.

$$q_{gas} = k_p (P_{gas,tot} - P_{atm}) * \frac{P_{gas}}{P_{atm}} \quad \text{.....(5.16)}$$

$P_{gas,\ tot}$ is the sums of partial pressures for all gases in the digester (eq. 5.13) and q_{gas} the total gas flow. $P_{gas,\ tot}$ and q_{gas} both include water vapour. An expression for water vapour partial pressure is given in Batstone et al (2002) and was used. It is given by the equation (5.14). P_{atm} is the atmospheric pressure, set to1.1013. Gas pressures are in bar. k_p is the pipe resistance coefficient in $m^3/d/bar$ for calculating the gas flow according to Batstone et al., (2002b). The gas flow is not only depending on the difference in pressure (ΔP) but might be restricted by an orifice, k_p must therefore be chosen according to the outlet of the biogas and the reactor volume.

$$P_{gas,total} = P_{gas,CH_4} + P_{gas,CO_2} + P_{gas,H_2} + P_{gas,H_2O} \quad \text{.....(5.17)}$$

$$P_{gas,H_2O} = 0.0313.\exp\left(5290 \cdot \left(\frac{1}{298} - \frac{1}{T}\right)\right) \quad \text{.....(5.18)}$$

Liquid phase physico-chemical equations are implemented as dynamic equations. The biochemical process parameters and physiochemical constants used in the model partly come from ADM1, and partly from Feng (2004). The proposed model has 34 dynamic state variables, consider both biochemical and physicochemical processes and contains several inhibition factors including 3 gas components. The number of processes considered is 28. The structure of the modified ADM1 model in the Peterson matrix form is shown in Table 5.5 and 5.6.

Table 5.5 Matrix of biochemical and physiochemical process (modified from ADM1)

j	Component i Process	1 S_{su}	2 S_{aa}	3 S_{fa}	4 S_{bu}	5 S_{pro}	6 S_{ac}	7 S_{h2}	8 S_{ch4}	9 S_{co2}	10 S_{nh3}	11 S_I	12 S_{va-}	13 S_{bu-}	14 S_{pro-}	15 S_{ac-}	16 S_{hco3}	17 S_{nh4}	Rate(p_i, kg COD.m^{-3}.d^{-1})
1	Disintegration											0.05							$4.5*X_c$
2	Hydrolysis carbohydrates	1																	$10*X_{ch}$
3	Hydrolysis protein		1																$10*X_{pr}$
4	Hydrolysis lipid	0.05																	$10*X_{li}$
5	Uptake of sugar	-1			0.12	0.24	0.37	0.17		7.2E-3	-6.2E-4								$30\frac{S_{su}}{0.5+S_{su}}X_{su}I_1$
6	Uptake of amino acid		-1	0.21	0.24	4.6E-2	0.37	5.5E-2		3.7E-3	6.5E-3								$50\frac{S_{aa}}{0.3+S_{aa}}X_{aa}I_1$
7	Uptake of lcfa						0.66	0.28			-3.7E-4								$6\frac{S_{fa}}{0.4+S_{fa}}X_{fa}I_2$
8	Uptake of valerate			-1			0.29	0.14			-3.7E-4								$18\frac{S_{va}}{0.11+S_{va}}X_{c4}\frac{1}{1+S_{bu}/S_{va}}I_2$
9	Uptake of butyrate				-1		0.75	0.19			-3.7E-4								$18\frac{S_{bu}}{0.11+S_{bu}}X_{c4}\frac{1}{1+S_{va}/S_{bu}}I_2$
10	Uptake of propionate					-1	0.55	0.41		8.4E-3	-2.5E-4								$14\frac{S_{pro}}{0.12+S_{pro}}X_{pro}I_2$
11	Uptake of acetate						-1		0.95	1.5E-2	-3.1E-4								$13\frac{S_{ac}}{0.16+S_{ac}}X_{ac}I_3$
12	Uptake of hydrogen							-1	0.94	-1.6E-2	-3.7E-4								$35\frac{S_{h2}}{0.000007+S_{h2}}X_{h2}I_1$
13	Decay of Xsu																		$0.03*X_{su}$
14	Decay of Xaa																		$0.03*X_{aa}$
15	Decay of Xfa																		$0.02*X_{fa}$

		Monosaccharides (kgCOD.m^{-3})	Amino acids (kgCOD.m^{-3})	Total valerate (kgCOD.m^{-3})	Total butyrate (kgCOD.m^{-3})	Total propionate (kgCOD.m^{-3})	Total acetate (kgCOD.m^{-3})	Hydrogen in liquid (kgCOD.m^{-3})	Methane in liquid (kgCOD.m^{-3})	Carbon dioxide in liquid (kmole.m^{-3})	Ammonia (kmole.m^{-3})	Soluble inert (kgCOD.m^{-3})	Valerate (kgCOD.m^{-3})	Butyrate (kgCOD.m^{-3})	Propionate (kgCOD.m^{-3})	Acetate (kgCOD.m^{-3})	Bicarbonate (kgCOD.m^{-3})	Ammonium (kgCOD.m^{-3})	Inhibition factors: $I_1 = I_{pH,Ul,Im}$ $I_2 = I_{pH,Ul,Im} I_{h2}$ $I_3 = I_{pH,Ul,Im} I_{NH3,XAC}$
16	Decay of Xc4																		$0.03*X_{c4}$
17	Decay of Xpro																		$0.04*X_{pro}$
18	Decay of Xac																		$0.04*X_{ac}$
19	Decay of Xh2																		$0.04*X_{h2}$
20	Valerate acid-base												-1						$10^8[S_{va\_}S_{h_+} - 1.58 * 10^{-5}(S_{va}/208 - S_{va\_})]$
21	Butyrate acid-base													-1					$10^8[S_{bu\_}S_{h_+} - 1.44 * 10^{-5}(S_{bu}/160 - S_{bu\_})]$
22	Propionate acid-base														-1				$10^8[S_{pro\_}S_{h_+} - 1.31 * 10^{-5}(S_{pro}/112 - S_{pro\_})]$
23	Acetate acid-base															-1			$10^8[S_{ac\_}S_{h_+} - 1.73 * 10^{-5}(S_{ac}/64 - S_{ac\_})]$
24	Inorg.carbon acid-base									1							-1		$10^8[S_{hco3}S_{h_+} - (4.46 * 10^{-7} * S_{co2}]$
25	Inorg.nitrogen acid-base										-1							1	$10^8[S_{nh3}S_{h_+} - (5.62 * 10^{-10} * S_{nh4}]$
26	CO2 gas stripping									-1									$10^4[S_{co2} - (0.035 * CO_{2,gas} * 0.08314 * T]$
27	H2 gas stripping							-16											$10^4[S_{h2}/16 - (0.00078 * H_{2,gas} * 0.08314 * T]$
28	CH4 gas stripping								-64										$10^4[S_{ch4}/64 - (0.0014 * CH_{4,gas} * 0.08314 * T]$

Table 5.6 Matrix of biochemical and physiochemical process (continued)

j	Component i / Process	18 X_c	19 X_{ch}	20 X_{pr}	21 X_{li}	22 X_{lcfa}	23 X_{su}	24 X_{aa}	25 X_{fa}	26 X_{c4}	27 X_{pro}	28 X_{ac}	29 X_{h2}	30 X_I	31 CO_{2gas}	32 $H_{2\,gas}$	33 CH_{4gas}	34 Alk	Rate(ρ_j, kg COD.m^{-3}.d^{-1})
1	Disintegration	-1	0.2	0.35	0.35									0.05					$4.5*X_c$
2	Hydrolysis carbohydrates		-1																$10*X_{ch}$
3	Hydrolysis protein			-1															$10*X_{pr}$
4	Hydrolysis lipid				-1	0.95													$10*X_{li}$
5	Uptake of sugar						0.1												$30\frac{S_{su}}{0.5+S_{su}}X_{su}I_1$
6	Uptake of amino acid							0.08											$50\frac{S_{aa}}{0.3+S_{aa}}X_{aa}I_1$
7	Uptake of lcfa					-1			0.06										$6\frac{S_{fa}}{0.4+S_{fa}}X_{fa}I_2$
8	Uptake of valerate									0.06									$18\frac{S_{va}}{0.11+S_{va}}X_{c4}\frac{1}{1+S_{bu}/S_{va}}I_2$
9	Uptake of butyrate									0.06									$18\frac{S_{bu}}{0.11+S_{bu}}X_{c4}\frac{1}{1+S_{va}/S_{bu}}I_2$
10	Uptake of propionate										0.04								$14\frac{S_{pro}}{0.12+S_{pro}}X_{pro}I_2$
11	Uptake of acetate											0.05							$13\frac{S_{ac}}{0.16+S_{ac}}X_{ac}I_3$
12	Uptake of hydrogen												0.06						$35\frac{S_{h2}}{0.000007+S_{h2}}X_{h2}I_1$
13	Decay of Xsu	1					-1												$0.03*X_{su}$
14	Decay of Xaa	1						-1											$0.03*X_{aa}$
15	Decay of Xfa	1							-1										$0.02*X_{fa}$

		Composites (kgCOD.m^{-3})	Carbohydrates (kgCOD.m^{-3})	Proteins (kgCOD.m^{-3})	Lipids (kgCOD.m^{-3})	Long chain fatty acids (kgCOD.m^{-3})	Sugar degraders (kgCOD.m^{-3})	Aminoacid degraders (kgCOD.m^{-3})	LCFA degraders (kgCOD.m^{-3})	Valerate and Butyrate degraders (kgCOD.m^{-3})	Propionate degraders (kgCOD.m^{-3})	Acetate degraders (kgCOD.m^{-3})	Hydrogen degraders (kgCOD.m^{-3})	Particulate inerts (kgCOD.m^{-3})	Carbon dioxide gas (kmole.m^{-3})	Hydrogen gas (kmole.m^{-3})	Methane gas (kmole.m^{-3})	Alkalinity(kmole.m^{-3})	Inhibition factors: $I_1 = I_{pH,In,lim}$ $I_2 = I_{pH,In,lim}\ I_{h2}$ $I3 = I_{pH,In,lim}I_{NH3,XAC}$
16	Decay of Xc4	1								-1									0.03*X_{c4}
17	Decay of Xpro	1									-1								0.04*X_{pro}
18	Decay of Xac	1										-1							0.04*X_{ac}
19	Decay of Xh2	1											-1						0.04*X_{h2}
20	Valerate acid-base																		$10^8[S_{va\_}S_{h_+} - 1.58 * 10^{-5}(S_{va}/208 - S_{va\_})]$
21	Butyrate acid-base																		$10^8[S_{bu\_}S_{h_+} - 1.44 * 10^{-5}(S_{bu}/160 - S_{bu\_})]$
22	Propionate acid-base																		$10^8[S_{pro\_}S_{h_+} - 1.31 * 10^{-5}(S_{pro}/112 - S_{pro\_})]$
23	Acetate acid-base																		$10^8[S_{ac\_}S_{h_+} - 1.73 * 10^{-5}(S_{ac}/64 - S_{ac\_})]$
24	Inorg.carbon acid-base																		$10^8[S_{hco3}S_{h_+} - (4.46 * 10^{-7} * S_{co2}]$
25	Inorg.nitrogen acid-base																		$10^8[S_{nh3}S_{h_+} - (5.62 * 10^{-10} * S_{nh4}]$
26	CO2 gas stripping														1				$10^4[S_{co2} - (0.035 * CO_{2,gas} * 0.08314 * T]$
27	H2 gas stripping															1			$10^4[S_{h2}/16 - (0.00078 * H_{2,gas} * 0.08314 * T]$
28	CH4 gas stripping																1		$10^4[S_{ch4}/64 - (0.0014 * CH_{4,gas} * 0.08314 * T]$

5.4 Model Implementation

The model is coded and implemented using the MATLAB® version 7.11.0.584(R 2010b). MATLAB is an interpreted programming language and therefore debugging is simplified. ADM1 is usually implemented with higher level software using graphical interfaces (eg. SIMULINK), thus avoid code-writing. But in this thesis, the model is programmed using only MATLAB primitives, giving greater flexibility in programming and speed, at the cost of user friendliness. The Matlab is a vector oriented programming language i.e., each variable is automatically taken to be a vector, and common vector operations such as vector addition, matrix multiplication, transpose etc., are defined at primitive level. MATLAB also provides a large number of built-in subroutines to solve several types of mathematical problems. Several subroutines are available for solution of systems of ordinary differential equations and graphing of results. The vector nature of the variables allows generation of compact and legible code and fast computation.

The model is a set of first order ordinary differential equations representing material balances and an algebraic equation (polynomial) representing charge balance. It is an explicit initial value ODE problem of the form:

$$y' = f(y,t)$$

$$y(t_o) = y_0$$

Where,

y is a dependent variable vector of a single independent variable t,

i.e., y= $\{y_1, y_2, \ldots\}$, each y_i being a function of t

y' is a vector denoting the dy/dt

y_0 is given data at t_0 (initial value)

The model equations are a set of ordinary differential equations with widely varying rates. In mathematics, the set of equations is termed stiff. It refers to time dependent systems where the dependent variables have widely different time scales, or where the solution has regions of slow evolution in time and spurts of rapid change. When solving stiff differential equations, the solutions do not converge unless time steps are chosen very carefully. A change is termed rapid, if the time scale of the change is very short compared with the time scale of integration. For instance, in anaerobic digestion, the time scale for the acid-base reaction, the formation of carbon dioxide from bicarbonate is very short, as compared with bacterial growth or enzymatic hydrolysis. Hence modelling carbon dioxide formation from bicarbonate as a rate process rather than as a equilibrium ratio could make convergence very slow or impossible for some numerical solvers. Ordinary differential equation is solved by using Euler method solver ODE15s, which can, to an extent, speed up the solution.

ODE15s solve stiff differential equations and differential algebraic equations (DAEs), variable order method. Syntax of ODE 15s is as follows:

[Tout, Yout] = ode15s (odefun, tspan, y0) with tspan = [t0 tfinal] integrates the system of differential equations y' = f(t,y) from time t0 to t final with initial conditions y0. ODEFUN is a function handle. For a scalar T and a vector Y, odefun (T,Y) must return a column vector corresponding to f(t,y). Each row in the solution array Yout corresponds to a time returned in the column vector Tout. To obtain solutions at specific times t0, t1,...,tfinal (all increasing or all decreasing), use tspan = [t0, t1 ... ,tfinal].

5.5 Model Simulation

The developed model is simulated for the mesophilic AD of OFMSW for continuous process. The input characterisation is a critical step in modelling anaerobic digestion. The model is simulated at the OLR of 3.1 kg VS/m^3/d. The inlet volatile solid concentration was 3.1 kg VS/m^3 with approximately 72% of particulate matter. The conversion of VS to COD is given in Table 5.3. We assume that the soluble COD is mainly composed of sugars. COD distribution of OFMSW is given in Table 5.4. The model parameters need to be adjusted to meet expected behaviour. The total volume of the digester was 36.8 L and the gas headspace volume was 7.4 L. The comparison of the actual and the adapted model predictions for pH value, gas production and biogas yield is summarized in Figure 5.3 to 5.5. It can be seen that the model was able to predict the pH value, gas production and biogas yield with considerable accuracy.

The comparison between experimental and simulated pH is shown in the Figure 5.3. The actual pH ranged between 7.15 and 7.6 while the pH predicted by the ADM1 ranged between 7. 05 and 7.7. It was noticed that there is slight variation of simulated result with the experimental values. This deviation may be caused by the following reasons:

- The reactor is assumed to be in a completely mixed state in the model, which is hard to achieve.
- The values of kinetic parameters of this model were determined from different references.
- Moreover, the substrate distribution between proteins, carbohydrates, and lipids was not measured but default model values were adopted from literature.

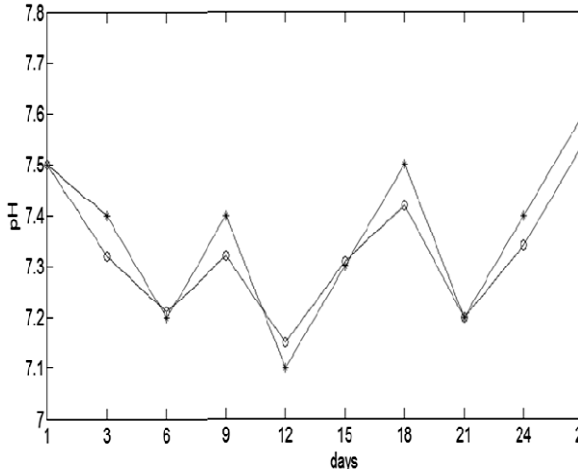


Figure 5.3 Comparison between the simulated and the experimental pH

The variation of the biogas production with time is shown in Figure 5.4. The biogas production clearly depends on the nature, composition, and biodegradability of the waste. The actual biogas production value ranged between 7.8 L/day and 61.8 L/day, the predicted biogas production value by ADM1 ranged between 7.7 L/day and 62.5 L/d. It is noticed that simulated result is a quite good agreement with the experimental values. The comparison between experimental and simulated specific biogas production is shown in the Figure 5.5. The actual biogas yield obtained at the end of 30 days digestion was 368 L/kg VS fed, but the predicted value by ADM1 was 369 L/kg VS. It is noticed that simulated result is a quite good agreement with the experimental values.

Simulated result of biogas composition is shown in the Figure 5.6, which is composed of methane gas, carbon dioxide, and hydrogen. However, since the hydrogen volume is not important it was set as zero in the total volume and it was assumed that the gas is only made of methane and carbon dioxide. The results showed that the biogas contains 65% methane and 35% CO_2.

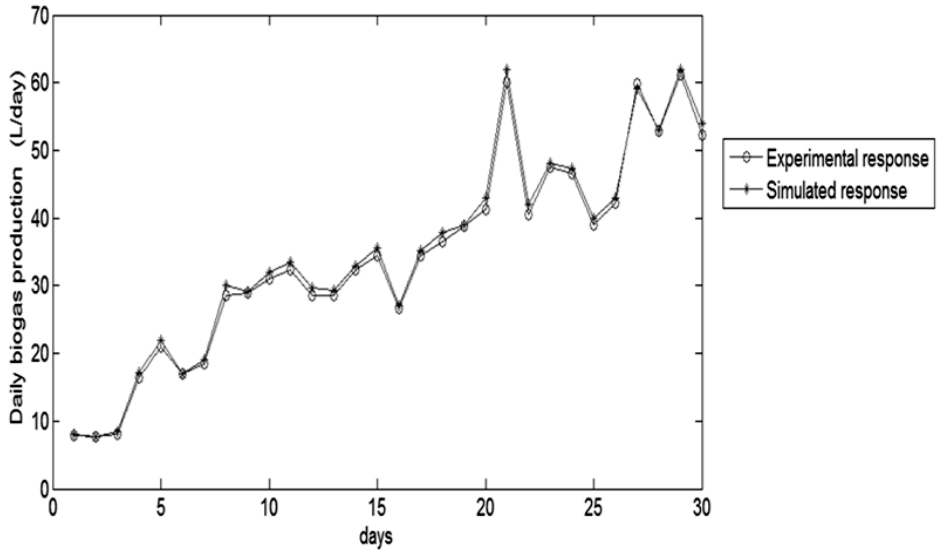


Figure 5.4 Comparison between the simulated and the experimental biogas production rate

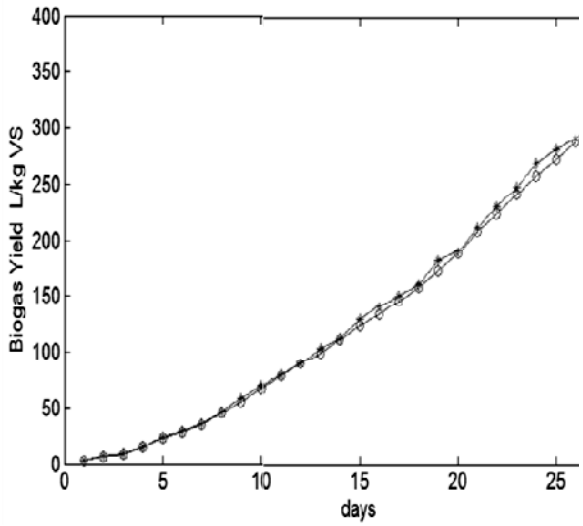


Figure 5.5 Comparison between the simulated and the experimental biogas yield

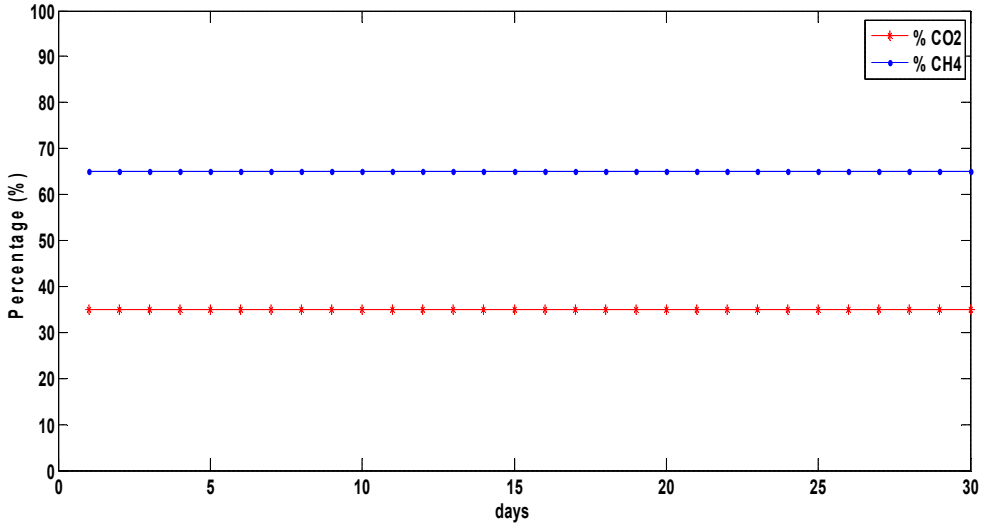


Figure 5.6 Simulated biogas compositions

5.6 Conclusions

The model based on adapted ADM1 was tested to simulate the behaviour of a bioreactor for the mesophilic anaerobic digestion of OFMSW at OLR of 3.1kg VS/m^3/d. ADM1 showed acceptable simulating results, regarding the number of parameters involved and processes considered. In fact it cannot reproduce the intimate variations of the different parameters, but an average trend is exhibited. This can be explained by the fact that not all the input kinetic parameters are obtained via analyses but extracted from the literature. For the present case, the obtained experimental results can be tested for the prediction of different operating parameters. ADM1 can, therefore, be used as a managing tool of anaerobic digestion. The simulated results show an acceptable fit. Because of the ease of use and applicability, the adapted ADM1 model is recommended for the simulation of the performance of anaerobic digestion of OFMSW in continuous process at any organic loading rates.

Chapter 6

CONCLUSIONS

Contents

6.1 Conclusions

This research was conducted to develop feasible semi-dry anaerobic digestion process for the treatment of OFMSW for potential energy recovery and sustainable waste management. The experiments were performed in three major phases to achieve these objectives, and can be described as phase I (batch study for AD of OFMSW at mesophilic temperature at different substrate concentration), phase II (batch study for AD of OFMSW at thermophilic temperature) and phase III (bench scale study for continuous digestion). The main conclusions are summarized as follows:

Conclusions of batch study at mesophilic temperature

- At the end of the 100 days digestion, the biogas yield at TS concentrations of 115 g/l, 99 g/l and 83 g/l were 22.7, 55.9 and 43.1 L /kg VS respectively.

- On increasing the substrate concentration, the biogas production was reduced which may be due to accumulation of large amount of substrate and on decreasing the substrate concentration, the production was reduced which may be due to lack of substrate.
- Volatile solid degradation of 20.2 %, 45.2 % and 37.3 % were obtained during the loading in reactors at TS concentrations of 115 g/l, 99 g/l and 83 g/l respectively.
- The values of reaction rate constant, k, calculated for the reactors at TS concentrations of 115 g/l, 99 g/l and 83 g/l using first order kinetics were 0.0196, 0.0292 and 0.0319 (day^{-1}) respectively.
- The low C/N weight ratio in the digested substrate indicates that it can be utilised as bio fertilizer or soil conditioner.
- Response Surface Methodology using Central Composite Design with the Design-Expert Software optimized the process parameters such as substrate concentration, initial pH and TOC for the maximal biogas production. Only the initial pH and substrate concentration had significant individual effects on biogas yield. The interactive effects for all of these factors were found to be insignificant ($p > 0.05$).The optimum conditions for maximizing the biogas yield were a substrate concentration of 99 g/l, an initial pH of 6.5 and TOC of 20.32 g/l. Under this optimised condition, the maximum biogas yield was 53.4 L/kgVS.
- AD of OFMSW with optimized substrate concentration of 99 g/l (TS-10.5%) is a semi-dry digestion system.

Conclusion of batch study at thermophilic temperature

- Semi-dry batch anaerobic digestion of OFMSW was carried out for 45 days at 50°C. At the end of the digestion, approximately 3520 ml the biogas was produced.
- Biogas yield and kinetic constant were obtained as 52.9 L/kgVS and 0.0249 day^{-1}.
- About 66.7% of the total volatile matter in the substrate was converted during this semi-dry digestion.
- The low C/N weight ratio in the digested substrate indicates that it can be utilised as bio fertilizer or soil conditioner.

Conclusion of bench scale study (continuous process)

- An effective start-up of the anaerobic digestion with inoculum was done successfully.
- From the study, it is found that on increasing the loading rate, the biogas production decreased. The specific biogas production rate of 368, 229 and 130 L/kg VS fed were found in loading rate 3.1, 4.2 and 5.65 kg VS/m^3/d respectively.
- Volatile solid reductions of 65.9 %, 55.2 % and 43.7 % were obtained during the loading rates 3.1, 4.2 and 5.65 kg VS/m^3/d respectively.
- The highest VS degradation of 65.9% was obtained with OLR of 3.1 kg VS/m^3/d at a retention time of 30 days.
- From the present study the optimum loading rate obtained for maximum biogas production was 3.1 kg VS/m^3/d.

- The experimental results showed that the end product (digestate) of anaerobic digestion is relatively stable. C: N ratio of digested substrate was in the range 12:1–14:1, which is considered to be stable and high quality compost.

Conclusion of modelling and simulation

- A dynamic mathematical model based on the default ADM1 model (Adapted ADM1) for the mesophilic anaerobic digestion of OFMSW at OLR 3.1 kg VS/m^3/d was developed to gain insight into the processes inside the reactor**.**
- ADM1 showed acceptable simulating results, regarding the number of parameters involved and processes considered.
- The simulated results show an acceptable fit.
- Because of the ease of use and applicability, the adapted ADM1 model is recommended for the simulation and modelling of the anaerobic digestion of OFMSW at any organic loading rates.

6.2 Limitations of the Study

The following are the limitations of the study:

- Source segregation of organic fraction of solid waste.
- No strict control of temperature was done in the laboratory experiments during mesophilic anaerobic digestion. The experiments were conducted at room temperature, which was monitored to be in a normal range of 29-33^{o}C.

6.3 Scope for Future Research

From the results and the observations during this study, several recommendations can be proposed. Following are the scope for future research:

- Study the performance of single stage thermophilic semi-dry anaerobic digester in continuous system.
- Since the leachate obtained from digester still have high organic loadings, it would be feasible to treat the leachate from the single stage semi-dry digester with up flow Sludge Blanket Reactor (UASB) which should convert remaining volatile solids to biogas.
- In the present study only cow dung is used as the inoculum. The combination of inoculum such as cow dung and anaerobic sludge from other treatment plants should be investigated.
- Scale up of the bench scale reactor to pilot scale reactor for the treatment of AD of OFMSW.

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Annexures

Annexure I

SAMPLE CALCULATIONS

1. Moisture content, Total Solid (TS) and Volatile Solids (VS)

For Substrate Characteristics: (for batch study, refer table 4.1)

Weight of sample before drying = 53.77 g

Weight of sample after drying = 9.95 g

$$Moisture\ Content\ (MC)\ \% = \frac{Weight\ of\ sample\ before\ drying - Weight\ of\ sample\ after\ drying}{Weight\ of\ sample\ before\ drying}$$

$$MC(\%) = \frac{(53.77 - 9.95)}{53.77} * 100 = 81.5\%$$

Total Solid (%) = 100 – moisture content (%)

= 100 % -- 81.5%

= 18.5%

$$Volatile\ Solid\ (VS)\% = \frac{Net\ mass\ of\ sample\ after\ ignition\ at\ 550\ oC}{Net\ mass\ of\ sample\ before\ ignition}$$

Weight of sample and crucible after 105^{o}C	= 18.48 g
Weight of sample and crucible after 550^{o}C	= 16.518 g
Weight of crucible	= 16.29 g
Weight of sample after 105^{o}C	= 2.19 g
Weight of sample after 550^{o}C	= 0.228 g

$$VS\ (\%) = \frac{(2.19 - 0.228)}{2.19} * 100 = 89.6\%$$

Annexure II

Table A3 Biochemical rate coefficients ($v_{i,j}$) and kinetic rate equations (ρ_j) for soluble components ($i = 1 - 12$, $j = 1 - 19$)

j	Component → / Process ↓	i	1 S_{su}	2 S_{aa}	3 S_{fa}	4 S_{va}	5 S_{bu}	6 S_{pro}	7 S_{ac}	8 S_{h2}	9 S_{ch4}	10 S_{IC}	11 S_{IN}	12 S_I	Rate (ρ_j, kg COD.m^{-3}.d^{-1})
1	Disintegration													$f_{sI,xc}$	$k_{dis}X_c$
2	Hydrolysis carbchydrates		1												$k_{hyd,ch}X_{ch}$
3	Hydrolysis of prcteins			1											$k_{hyd,pr}X_{pr}$
4	Hydrolysis of lipids		$1-f_{fa,li}$		$1-f_{fa,li}$										$k_{hyd,li}X_{li}$
5	Uptake of sugars		−1				$(1-Y_{su})f_{bu,su}$	$(1-Y_{su})f_{pro,su}$	$(1-Y_{su})f_{ac,su}$	$(1-Y_{su})f_{h2,su}$		$-\sum_{i=9,11-24} C_i v_{i,5}$	$-(Y_{su})\,N_{bac}$		$k_{m,su}\frac{S_{su}}{K_S+S}X_{su}I_1$
6	Uptake of amino acids			−1		$(1-Y_{aa})f_{va,aa}$	$(1-Y_{aa})f_{bu,aa}$	$(1-Y_{aa})f_{pro,aa}$	$(1-Y_{aa})f_{ac,aa}$	$(1-Y_{aa})f_{h2,aa}$		$-\sum_{i=1-9,11-24} C_i v_{i,6}$	$N_{aa}-(Y_{aa})\,N_{bac}$		$k_{m,aa}\frac{S_{aa}}{K_S+S_{aa}}X_{aa}I_1$
7	Uptake of LCFA				−1				$(1-Y_{fa})$ 0.7	$(1-Y_{fa})$ 0.3			$-(Y_{fa})\,N_{bac}$		$k_{m,fa}\frac{S_{fa}}{K_S+S_{fa}}X_{fa}I_2$
8	Uptake of valerate					−1		$(1-Y_{c4})$ 0.54	$(1-Y_{c4})$ 0.31	$(1-Y_{c4})$ 0.15			$-(Y_{c4})\,N_{bac}$		$k_{m,c4}\frac{S_{va}}{K_S+S_{va}}X_{c4}\frac{1}{1+S_{bu}/S_{va}}I$
9	Uptake of butyrate						−1		$(1-Y_{c4})$ 0.8	$(1-Y_{c4})$ 0.2			$-(Y_{c4})\,N_{bac}$		$k_{m,c4}\frac{S_{bu}}{K_S+S_{bu}}X_{c4}\frac{1}{1+S_{va}/S_{bu}}I$
10	Uptake of propionate							−1	$(1-Y_{pro})$ 0.57	$(1-Y_{pro})$ 0.43		$-\sum_{i=1-9,11-24} C_i v_{i,10}$	$-(Y_{pro})\,N_{bac}$		$k_{m,pr}\frac{S_{pro}}{K_S+S_{pro}}X_{pro}I_2$
11	Uptake of acetate								−1		$(1-Y_{ac})$	$-\sum_{i=1-9,11-24} C_i v_{i,11}$	$-(Y_{ac})\,N_{bac}$		$k_{m,ac}\frac{S_{ac}}{K_S+S_{ac}}X_{ac}I_3$
12	Uptake of hydrogen									−1	$(1-Y_{h2})$	$-\sum_{i=1-9,11-24} C_i v_{i,12}$	$-(Y_{h2})\,N_{bac}$		$k_{m,h2}\frac{S_{h2}}{K_S+S_{h2}}X_{h2}I_1$
13	Decay of X_{su}														$k_{dec,Xsu}X_{su}$
14	Decay of X_{aa}														$k_{dec,Xaa}X_{aa}$
15	Decay of X_{fa}														$k_{dec,Xfa}X_{fa}$
16	Decay of X_{c4}														$k_{dec,Xc4}X_{c4}$
17	Decay of X_{pro}														$k_{dec,Xpro}X_{pro}$
18	Decay of X_{ac}														$k_{dec,Xac}X_{ac}$
19	Decay of X_{h2}														$k_{dec,Xh2}X_{h2}$
			Monosaccharides (kgCOD·m^{-3})	Amino acids (kgCOD·m^{-3})	Long chain fatty acids (kgCOD·m^{-3})	Total valerate (kgCOD·m^{-3})	Total butyrate (kgCOD·m^{-3})	Total propionate (kgCOD·m^{-3})	Total acetate (kgCOD·m^{-3})	Hydrogen gas (kgCOD·m^{-3})	Methane gas (kgCOD·m^{-3})	Inorganic carbon (kmoleC·m^{-3})	Inorganic nitrogen (kmoleN·m^{-3})	Soluble inerts (kgCOD·m^{-3})	Inhibition factors: $I_1 = I_{pH}I_{N,lim}$, $I_2 = I_{pH}I_{N,lim}I_{h2}$, $I_3 = I_{pH}I_{N,lim}I_{NH3,Xac}$

Table A4 Biochemical rate coefficients ($\nu_{i,j}$) and kinetic rate equations (ρ_j) for soluble components (i = 13 – 24, j = 1 – 19)

	Component →	i	13	14	15	16	17	18	19	20	21	22	23	24	Rate (ρ_j, kg COD.m^{-3}.d^{-1})
j	Process ↓		X_c	X_{ch}	X_{pr}	X_{li}	X_{su}	X_{aa}	X_{fa}	X_{c4}	X_{pro}	X_{ac}	X_{h2}	X_I	
1	Disintegration		-1	$f_{ch,xc}$	$f_{pr,xc}$	$f_{li,xc}$								$f_{xI,xc}$	$k_{dis}X_c$
2	Hydrolysis carbohydrates			-1											$k_{hyd,ch}X_{ch}$
3	Hydrolysis of proteins				-1										$k_{hyd,pr}X_{pr}$
4	Hydrolysis of lipids					-1									$k_{hyd,li}X_{li}$
5	Uptake of sugars						Y_{su}								$k_{m,su}\frac{s_{su}}{K_S+S}X_{su}I_1$
6	Uptake of amino acids							Y_{aa}							$k_{m,aa}\frac{s_{aa}}{K_S+S_{aa}}X_{aa}I_1$
7	Uptake of LCFA								Y_{fa}						$k_{m,fa}\frac{s_{fa}}{K_S+S_{fa}}X_{fa}I_2$
8	Uptake of valerate									Y_{c4}					$k_{m,c4}\frac{S_{va}}{K_S+S_{va}}X_{c4}\frac{1}{1+S_{bu}/S_{va}}I$
9	Uptake of butyrate									Y_{c4}					$k_{m,c4}\frac{S_{bu}}{K_S+S_{bu}}X_{c4}\frac{1}{1+S_{va}/S_{bu}}I$
10	Uptake of propiorate										Y_{pro}				$k_{m,pr}\frac{S_{pro}}{K_S+S_{pro}}X_{pro}I_2$
11	Uptake of acetate											Y_{ac}			$k_{m,ac}\frac{S_{ac}}{K_S+S_{ac}}X_{ac}I_3$
12	Uptake of hydrogen												Y_{h2}		$k_{m,h2}\frac{S_{h2}}{K_S+S_{h2}}X_{h2}I_1$
13	Decay of X_{su}		1				-1								$k_{dec,Xsu}X_{su}$
14	Decay of X_{aa}		1					-1							$k_{dec,Xaa}X_{aa}$
15	Decay of X_{fa}		1						-1						$k_{dec,Xfa}X_{fa}$
16	Decay of X_{c4}		1							-1					$k_{dec,Xc4}X_{c4}$
17	Decay of X_{pro}		1								-1				$k_{dec,Xpro}X_{pro}$
18	Decay of X_{ac}		1									-1			$k_{dec,Xac}X_{ac}$
19	Decay of X_{h2}		1										-1		$k_{dec,Xh2}X_{h2}$
			Composites (kgCOD.m^{-3})	Carbohydrates (kgCOD.m^{-3})	Proteins (kgCOD.m^{-3})	Lipids (kgCOD.m^{-3})	Sugar degraders (kgCOD.m^{-3})	Amino acid degraders (kgCOD.m^{-3})	LCFA degraders (kgCOD.m^{-3})	Valerate and butyrate degraders (kgCOD.m^{-3})	Propionate degraders (kgCOD.m^{-3})	Acetate degraders (kgCOD.m^{-3})	Hydrogen degraders (kgCOD.m^{-3})	Particulate inerts (kgCOD.m^{-3})	Inhibition factors: $I_1 = I_{pH}I_{IN,lim}$; $I_2 = I_{pH}I_{IN,lim}I_{h2}$; $I_3 = I_{pH}I_{IN,lim}I_{NH3,Xac}$

Publications

Journals

1) B. Sajeena Beevi.,G. Madhu., Deepak kumar Sahoo (2015) 'Performance and Kinetic Study of Semi-dry Thermophilic Anaerobic Digestion of Organic fraction of Municipal Solid Waste' *Waste Management*, Vol.36,2015,pp.93-97.

2) Sajeena Beevi.B., Jose P.P., Dr.G.Madhu (2014) 'Optimization of Process Parameters affecting Biogas Production from Organic Fraction of Municipal Solid Waste via Anaerobic Digestion' *International Journal of Environmental, Ecological, Geological and Mining Engineering.* Vol:8 No:1, 2014, pp.43-48.

3) Sajeena Beevi.B., Ajit Haridas., G.Madhu., Dipak Kumar Sahoo 'Performance Study of Anaerobic Digestion of Organic Fraction of Municipal Solid Waste in Mesophilic Continuous Operation'. *Renewable Energy*, published by Elsevier (under review)

4) B. Sajeena Beevi.,G. Madhu., Dipak kumar Sahoo 'Modelling and Simulations of Semi-dry Anaerobic Digestion of Organic Solid Waste in Mesophilic Conditions' *International Journal of Environment and Waste Management* (Inderscience publications) (Communicated)

Conferences

1) Sajeena Beevi.B and G. Madhu (2012) 'Dry Anaerobic Digestion Process for the Treatment of organic fraction of Municipal Solid Waste-A Review', *Proceedings of National conference on Advances in Manufacturing Systems and Processes,* Govt. Engineering College, Thrissur, India , pp.161-164,5-7 November 2012.

2) Jose P.P., Sajeena Beevi.B., Ushakumary E.R (2013) 'Anaerobic Digestion of Organic Fraction of municipal solid wastes: Kinetic study' *Proceedings of 1st National conference on Advanced Trends in Chemical Engineering*, Govt. Engineering College, Thrissur, India, pp.29-33, 26-28 September 2013.

3) Jose P.P., Sajeena Beevi.B., Ushakumary E.R (2013) 'Anaerobic Digestion of Organic Fraction of municipal solid wastes: Analytical approach' *Proceedings of 3 rd International Conference on Materials for Future ICMF 2013*, Govt. Engineering College, Thrissur, India,06-08 November 2013.

4) Sajeena Beevi.B., Jose P.P., Dr.G.Madhu (2014) 'Optimization of Process Parameters affecting Biogas Production from Organic Fraction of Municipal Solid Waste via Anaerobic Digestion' *In proceedings of International Conference on Biological and Environmental Engineering*, Hotel Crown Plaza, Dubai, UAE, supported by World Academy of Science ,Engineering and Technology, International Science Index,Vol.85, pp.995-1000,30-31 January 2014.

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