

**BIOGAS PRODUCTION THROUGH DRY ANAEROBIC DIGESTION OF
WASTE SLUDGE**



By

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List of Abbreviations

Abbreviation	Description
AD	Anaerobic Digestion
C/N Ratio Ratio	Carbon to Nitrogen
BOD Demand	Biological Oxygen
COD Demand	Chemical Oxygen
g	Gram
kg	Kilogram
mg/l	Milli gram per liter
OLR	Organic Loading Rate
HRT Time	Hydraulic Retention
TKN Nitrogen	Total Kjehldehl
TN	Total Nitrogen
TS	Total Solids
VS	Volatile Solids
VFA	Volatile Fatty Acids
ALK	Alkalinity
d	Day
⁰ C	Degree Celsius
L	Liter
m	Meter

Abstract

A single stage pilot scale anaerobic reactor of 50 Litter volume was constructed to conduct dry anaerobic co-digestion of sludge and rice husk. Reactor was started with batch start-up phase followed by semi-continuous phase. Total solid content and C: N ratio of waste mixture used in this research was maintained at 15% and 30 respectively. Mesophilic temperature range was maintained in reactor. Effect of variation in organic loading rates of biogas production was examined in semi-continuous phase. For this purpose the reactor was operated at OLR of 2, 4, 6 and 8 kg VS/m³/d. Results revealed that in comparison of OLR 2, 4 and 8 OLR 6 had higher biogas production rate. Average specific biogas yield of 142 L/kg/Vs with %VS removal of 63% was achieved. For OLR 2, 4 and 8 these were 113, 94, 115 and 76, 61, 47%. Reactor performance decreased with at OLR 8 due to Volatile fatty acids accumulation and inhibition of biogas production. Thus based on biogas production and stability of anaerobic reactor, OLR 6 kg VS/m³/d was considered to be most optimum for dry anaerobic co-digestion of waste sludge and rice husk.

Keywords: [Organic loading rate, specific biogas yield, Volatile fatty acids, mesophilic, biogas]

Chapter 1

Introduction

1.1 Background

Pakistan's population is growing and concentrating in urban centers. This tendency is mainly penetrating in developing countries, where a further 2.1 billion people are projected to be living in cities by year 2030. These cities produce billions of tons of waste every year, comprising of wastewater and sludge. The destiny of these wastes is quite dissimilar subjected on local situation: they can be picked or not, treated or not and finally used directly, indirectly or finish without convenient use. In literature, data on such waste streams is uncommon and disseminated and detailed analyses and calculations at international level are absent, with merely rare and fractional omissions. However, current efforts from international organizations like FAO/IWMI through UN-Habitat , AQUASTAT and Global Water Intelligence permit recommencing these calculations and giving a more updated analysis (Drechesel et al., 2015).

Domestic wastewater and sludge comprise useful resources such as energy, organic matter, water and nutrients which can be recuperated for different diverse social, economic and environmental purposes. Though, and as a result of the lacking global data on waste flows, the total quantity of resources that is recuperated for advantageous uses has not been well calculated till now. (Drechesel et al., 2015, Ødegaard et al 2002). Approximately 330 cubic kilometers per year of municipal wastewater is generated globally. The resources embedded in it are theoretically enough to irrigate and fertilize millions of hectares of crops and to generate biogas to supply energy for millions of households.

In Pakistan 3.06 cubic kilometer per year wastewater is generated out of which 0.55 cubic kilometers per year is treated generating 560 thousand metric ton of sludge. As unfortunately we have inadequate wastewater and waste management systems so the portion which is safely reused is significantly smaller and is posing significant potential health risks. So sustainable management of sludge is required.

Wastewater for 14 cities of our country, calculated on the foundation of 1998 population census, is nearly $1.83 \times 10^7 \text{ m}^3/\text{h}$ as shown in table 1 (Murtaza,G. et al., 2012,

PWSS., 2002). Latest projections reveal that total amount of wastewater produced in our country is 962,335 million gallons ($4.369 \times 10^9 \text{ m}^3/\text{yr}$) as well as 674,009 million gallons ($3.060 \times 10^9 \text{ m}^3/\text{yr}$; a figure of $5.54 \times 10^9 \text{ m}^3/\text{yr}$ for the year 2011).

Table 1 Sector wise estimated wastewater production in Pakistan

Sr. No.	Source	Volume	
		$10^6 \text{ m}^3/\text{year}$	Volume %
1	Industry	395	6
2	Commercial	266	5
3	Urban residential	1,628	25
4	Rural residential	3,059	48
5	Agriculture	1,036	16
	Total	6,414	100

From urban 288,326 million gallons ($1.309 \times 10^9 \text{ m}^3/\text{yr}$.) from industrial use. The total wastewater released to the major rivers is 392,511 million gallons ($1.782 \times 10^9 \text{ m}^3/\text{yr}$. and $1/3^{\text{rd}}$ of all wastewater), which comprises 316,740 million gallons. Details are mentioned in table 1 related to different sectors generating wastewater in Pakistan in Table 1. It is clear that urban and rural residential sectors comprise the highest percentage of wastewater generation in Pakistan.

In Pakistan, municipal waste comprising household effluent and human waste is either released nonstop a natural drain or water body, an internal septic tank, a nearby field, or to a sewer system. Usually, domestic wastewater is not exposed to any management and none of municipalities have any biological treatment method excluding Karachi and Islamabad, and even those municipalities treat merely a minor fraction of their wastewater prior to disposal. Supposing that all the mounted treatment setups are functioning at their full installed capability, it is projected that about 8% of municipal wastewater is possibly .treated in urban treatment setups (Murtaza et al., 2012) (Table 2). Cities in Pakistan being the epi-center of population are main sources of wastewater generation. Table 2 highlights major urban centers in Pakistan where most of population resides. The issue in Pakistan is not wastewater generation, but the lack of drainage, treatment and disposal facilities. Sludge in waste water accumulates in all of the channels wastewater flow through, by this

disease outburst is spread as well as inadequate management of sludge results in loss of valuable item for creating alternate energy.

Sludge is a material formed when suspended solids present in wastewater are converted

Table 2 Wastewater generated annually by cities of Pakistan

City	Urban population (1998 census)	Total wastewater produced $10^6\text{m}^3/\text{yr.}$	% of Total	% of Treated	Receiving water Body
Lahore	5,143,495	287	12.5	0.01	River Ravi, irrigation canals, vegetable farms
Faisalabad	2,008,861	129	5.6	25.6	River Ravi, River Chenab and vegetable farms
Gujranwala	1,132,509	71	3.1	-	SCARP drains, vegetable farms
Rawalpindi	1,409,768	40	1.8	-	River Soan and vegetable farms
Sheikhupura	870,110	15	0.7	-	SCARP drains
Multan	1,197,384	66	2.9	-	River Chenab, irrigation canals and farms
Sialkot	713,552	19	0.8	-	River Ravi, irrigation canals and farms
Karachi	9,339,023	604	26.3	15.9	Arabian Sea
Hyderabad	1,166,894	51	2.2	34.0	River Indus, irrigation canals and SCARP drains
Peshawar	982,816	52	2.3	36.2	Kabul River
Other	19,475,588	967	41.8	0.7	-
Total Urban	43,440,000	2,301	100.0	7.7	-

into soluble organic substances and bacterial biomass. The sources of sludge from wastewater treatment plant. The sludge is generated in sedimentation tanks; the same is recalcitrant in aeration tanks while the excess one is discharged into environment.

Table 2 highlights that the highest percentage of wastewater is generated from Karachi which is a city of 20 million. It also highlights the lack of capacity at city level to treat wastewater as well as the disposal bodies. This table provides overall scenario of situation related to wastewater mismanagement in Pakistan.

The sludge present in wastewater needs to experience certain management in order to lessen its volume, to progress its parameters and to decrease the related health and environmental difficulties and interference. This treatment will hence initially decrease the water content of the raw sludge, alter the highly decay able organic matter in comparatively non-degradable and stable inorganic and organic residue and finally form the residue to meet strict disposal values, meanwhile direct land use is problematic because of strict guidelines.(Appels et al., 2011).

Wastewater and sludge management issues are of immense importance but, Pakistan is an energy deficient country having limited options for this sector.

Sludge is generated from ETP but that is in liquid state. Initially it is thickened, dewatered and dried and then subjected to various treatments, the thermochemical ones like incineration, pyrolysis and gasification to the aerobic ones like digestion, composting and others.

Our area under consideration is anaerobic digestion i.e. breakdown of bio degradable sludge material in absence of oxygen by anaerobic bacteria. We prefer it as it is naturally economic, energy is generated in form of biogas and methane in particular and greenhouse gases are abated while the digestate obtained as a result of anaerobic digestion can be used as a fertilizer in agricultural field.

For economic and social progress if any society, energy is a vital component. In absence of ample amount of energy as usable forms and at manageable cost living conditions of people cannot be improved. Pakistan as an under developing country bear costs of nearly 7 billion dollars for importing fossil fuels on annual basis to meet its energy requirements. In Pakistan just 55% and 18% of households are provided with electricity and gas correspondingly. Provision of electricity/energy at commercial scale is among the lowest in the globe. Nearly 68% of inhabitants reside in villages and much do not have approach to energy (gas and electricity) and people use biomass like animal manure, agricultural waste and fire wood to fulfill their requirements.

In Pakistan power, transport, domestic and industrial sectors are major consumers of commercial energy. The power producing sector utilizes about 33% of gas, 38% of oil and coal consumption is 2% in country.

Main reason of our energy crisis is because of increasing requirement of energy because of increased population, urbanization and industrial setup. But our capability of provisions remains similar. The few reasons of this deficit are given below:

- New energy projects with enhance in demand are usually not established.
- Due to bad management and poor maintenance line losses are increasing day by day.
- Our power transmission setup being a conventional one cannot afford extra load more than its capability.
- In our country financial mismanagement in energy sector is very high.
- Government does not pay to independent power producing setup (IPPs).
- Circular debt rises annually and authorities have to put burden on people from people to pay arrears to independent power producing setup.

Our country is progressing underdeveloped country. So, it is essential for us to take exceptional measures to expedite its emerging economy. But because of it energy issue our economy hurts quite critically. The sustainable and renewable energy resources are most alternatives to energy sources and typical fuels (Appels et al., 2011)

Renewable resources have a dire role in reducing the emissions of CO₂. Energy through waste and biomass is considered as the most promising future renewable source of energy. A continuous power generation can be obtained through this source.

The potential energy worth from carbon present in wastewater could be predicted considering an anaerobic conversion factor for organic carbon to CH₄ of 0.14 m³ methane per m³ of wastewater, at 20°C, (Frinjs et al 2013; Verstraete et al 2009) seeing that the calorific worth of CH₄ is 35.9 MJ/m³CH₄.

The potential energy worth from carbon present in wastewater could be predicted considering an anaerobic conversion factor for organic carbon to CH₄ of 0.14 m³ methane per cubic meter of wastewater, at 20°C, (Frinjs et al 2013; Verstraete et al 2009) seeing that the calorific worth of CH₄ is 35.9 MJ/m³ CH₄. So, the 330 km³ of urban wastewater projected to be produced globally, assuming a medium strength wastewater, can potentially yield 46.2 km³ CH₄ with an international calorific value of 1660-109MJ, which, if completely recovered, would be sufficient to give energy for about 130 million homes, since an average electricity utilization of 3500 kWh/household (World Energy Council

2013). Pakistan being a population of nearly 220 million and generating wastewater of 3.06 km³ can extract ample amount of energy as estimated sludge content can be 560 thousand metric tons annually (Sagasta et al., 2015).

Based on these facts, the use of anaerobic digestion has emergent amazingly. Anaerobic digestion of sludge is done in airtight tanks. Organic matter can be digested, only the stable woody materials as the anaerobic microbes cannot to digest lignin. The biogas that is generated has a high caloric value and is referred as a renewable source of energy. Undoubtedly, it is useful to produce as much biogas as possible.

The potential of using the biogas as energy source has been widely studied and recognized. Current techniques are being developed to upgrade quality of energy generated and to enhance energy use. (Libhaber and Orozco-Jaramillo 2013). A resourceful energy material is methane. Methane is a carbon-based gas primarily made from biological reactions. One of these biological reactions is anaerobic digestion that place without the occurrence of oxygen by microorganisms.

Anaerobic digestion takes place when bacteria convert a biomass feedstock into various other organic compounds, finally changing in a mixture of carbon dioxide and methane called biogas. By fraction the biogas contains 60% methane and 40% CO₂ with traces of other gases. Whereas carbon dioxide generated due to human activities is an apprehension with emissions of greenhouse gas, the carbon dioxide released in this response is assumed carbon neutral. Methane can be filtered and used for generating heat or electricity (World Energy Council 2013). AD serves a dual purpose in both reduction in volatile solids and providing methane, dropping the risk of possible pollution when the slurry is discarded. The solids can too be used for numerous agricultural purposes like fertilizers.

There are two types by which anaerobic digestion can be classified. Dry anaerobic digestion and wet anaerobic digestion. In dry anaerobic digestion reactor volume is kept smaller as volume of feed is lower and solid content is higher in range of 15-40%. In wet digestion, reactor size is larger as volume of feed is high and solid content is comparatively lower as < 10%. So for sludge as it has volume, dry anaerobic digestion is preferred.

Also sludge has high nitrogen resultantly low C: N ratio that inhibits its direction due to ammonia-nitrogen accumulation, this problem is countered by addition of any material readily available and having low nitrogen and high carbon content resultantly high C:N

ratio. Pakistan being an agricultural country has abundance of agricultural waste, either its disposal is an issue. So rice straw, wheat straw, rice husk or any of material can be used for this purpose. This mixing of feed for AD is called co-digestion.

1.2 Objectives of the study

The key objective of this study is to acclimatize process, functioning of dry anaerobic co-digestion process treating domestic wastewater sludge by mixing it with rice husk (for attaining adequate feedstock's C/N ratio), at different rates of organic loading. This research will lead towards more innovation regarding anaerobic digestion through adequate selection of feed and will use these combinations for energy generation as well as management of solid waste domestic sludge which has ultimately to cause a management issue in Pakistan.

The objectives of this study are:

- To design and operate single stage semi-continuous mesophilic reactor for dry anaerobic co-digestion of sludge and rice husk
- To analyze the effects of organic loading rate on dry anaerobic co-digestion of sludge and rice husk.

1.3 Scope of the study

The research is carried out at pilot scale with a reactor of 50 liter volume with substrate of sludge and rice husk and inoculum source as cow dung and digestate from another anaerobic reactor. The anaerobic reactor from which inoculum digestate is taken is located in Bara Kahu, Islamabad. Sludge is obtained from a membrane bio reactor located at NUST, H-12 Islamabad and rice husk is obtained from Faisalabad, Pakistan. Study period is divided in two parts i.e. start-up phase and semi-continuous phase. Mesophilic temperature range is considered throughout the study span. After stabilization for 87 days in start-up phase, reactor is operated for 232 days in semi-continuous phase for determination of optimum organic loading rate for dry anaerobic digestion of sludge and rice-husk.

Chapter 2

Literature Review

In this section, detailed literature on the anaerobic digestion is reviewed. Multiple factors that affect anaerobic digestion are discussed in detail.

2.1 Anaerobic digestion

Bio-energy generation through anaerobic digestion of organic feedstock is an auspicious climate change mitigation choice and it is termed as a sustainable treatment tool to combat climate change. (Rajgopal et al., 2013).

In reality, bioenergy is assessed to be the 4th chief energy resource of world (Chen et al., 2014). Anaerobic setups are in place for treating and stabilization of wastewater sludges for decades. Relative benefits of anaerobic digestion comprise of: capacity to stabilize immense organic loadings; lower the amount formation of biomass; generation of a consumable fuel (methane biogas); and generation of stabile sludge, for which post-treatment innovations can be related to recover nutrients. AD is biological process which includes degeneration of inorganic and organic matter without absence of oxygen. Additionally, from a social and economic point of view, biogas not only expressively decreases the expenses of treating waste but too has a comparatively little cost of feedstock (Holem et al., 2013). Different categories of bacteria work on the organic feedstock and change it in final output like carbon-dioxide, ammonia and methane. The process occurs in 4 steps which are hydrolysis, acidogenesis, acetogenesis and methanogenesis these phases include significant and complicated synergy among bacteria that are basic to favorable working of methanogens.

In initial step high molecular weight compounds such as, polysaccharides lipids, and nucleic acids proteins and insoluble organic constituent are neutralized in soluble materials (e.g. sugars, fatty acids and amino acids) due to impact by different extracellular enzymes like proteases, ammonylases and cellulases are generated due

fermentative bacteria. These ingredients which are generated in hydrolysis further dismantle in the step of acidogenesis and come in production of volatile fatty acids with CO_2 , H_2S , ammonia and further by-products. Third step is acetogenesis in which these intermediary volatile fatty acids further digest by the acetogenic microbes to form direct methane precursor acetic acid and H_2 . Differential pressure of hydrogen gas in the blend dominates this reaction and thus the formation of Hydrogen gas by anaerobic oxidation is quite vital for proper working of anaerobic operations. In concluding phase of methanogenesis, methanogenic bacteria change the formerly formed hydrogen and acetic acid into carbon dioxide and methane gas. (Bowen et al., 2014). Two kinds of methanogenic groups are concerned in to it. Acetic methanogenic microbes convert acetic acid in carbon dioxide and methane. Microbes involved in oxidizing hydrogen use hydrogen as electron donor and carbon dioxide as an electron acceptor to generate CH_4 (Appels et al., 2011). Methanogenic bacteria are firm anaerobes that have quite slow rate of growth, consequently their metabolic activity normally measure rates of dissimilar phases of anaerobic digestion. As a result, their metabolism is usually measured rate-limiting and a long detention time is necessary for growth. Within the anaerobic environment, a range of important parameters influence the rates of the dissimilar steps of the digestion course, i.e. pH and alkalinity, temperature, and retention times. For effectual efficiency of an anaerobic digestion system these parameters must be maintained at finest levels and the generation of poisonous and inhibitory substances must be withdrawn. Apart from process efficiency different types of feedstock combinations can too be used for achieving better results in terms of biogas generation. (Borowski et al., 2014).

2.2 Types of digestion

Based on total solid contents anaerobic digestion is divided in two parts i.e. dry anaerobic digestion and wet anaerobic digestion. If total solid content is lesser than 10% then the digestion is wet anaerobic digestion. If total solid content is between 15-40% then digestion is termed in dry anaerobic digestion. The details of both types of digestion are mentioned below.

A key difference among anaerobic digestion (AD) for treatment of industrial and municipal biodegradable waste feedstock is operational process's solids concentration. Dry systems have higher operating solids (20→40% TS) and wet anaerobic digestion systems work at lower total solids (<10–20% TS). The operation of dry and wet setups had been measured relative to: technical operation (footprint, capacity, feed-stock characteristics, post-treatment and pretreatment, water usage), retention time, methane [CH₄] concentration, utilization of biogas and generated energy), specific capital costs[per ton of waste and per m³ biogas), energy balance (biogas generation, parasitic energy digestate management and financial performance (capital and operational costs, revenues,. Wet anaerobic digestion plants had economic performance and better energy balance as compared to dry anaerobic digestion plants. Though, dry anaerobic digestion setups offer various advantages that include greater flexibility in the type of feedstock acceptance, smaller retention times, decreased water consumption and more elastic management of and chances for marketing, the outcome. (Angelonidi et al., 2015)

2.3 Co-digestion of biomass

Rice wastes are among agricultural wastes that are taken as source of energy, particularly in countries where growth of cotton is at massive scale like China, Brazil, US, India, Australia, Pakistan, and Turkey. Amongst other rice wastes, rice husk has high lignocellulose content (60%). Lignocellulose is polysaccharide mixture of hemicelluloses, lignin and cellulose which has indigestible plant content. In Pakistan enormous quantities of agriculture related waste is generated. Rice husk is among them nearly 1.78 million tons on annual basis. (Mirani et al., 2013).

Co-digestion is employed for adjustment of carbon to nitrogen ratio of feed. Through co-digestion biogas generation is enhanced because of synergism generated in reactor and because of availability of nutrients unavailable in digestion medium from any constituents of co-substrate. It is proposed for AD dry addition up to 3 organic feeds can give a feedstock that has ample nutrients (Zhang et al., 2013). Also the use of same equipment in co-digestion gives financial advantages. In addition, variation in moisture content or TS of substrate is too resulted through co-digestion. Recently

agricultural waste and sludge are normally used for discussed purpose that is a smart option for many scholars.

Co-digestion of animal manure and agricultural waste has too produced adequate results for anaerobic digestion and this is because carbon to nitrogen ratio is maintained by addition of agricultural wastes like rice husk. (Wang et al., 2014).

Co-digestion of agricultural leftover along with feed that has high nitrogen (Sludge, food processing industry leftover, slaughter house waste etc) is established as useful as it can be used to adjust carbon to nitrogen ratio of overall substrate. Mixing of agricultural waste like rice husk us employed to control dry anaerobic digestion (Xiaojiao et al., 2014) as it controls accumulated volatile fatty acids and ammonia. In order to form most optimum feedstock different research scientists. In literature it is reported that combined 2-6% paper leftover, other 5 to 8% readily biodegradable feedstock (e.g. straw, fallen leaves and wood chips) along with 86 to 93% of different feeds like food, fruit, and vegetable waste that had a potential of adjustment of generation and buildup of volatile fatty acids (Liew et al., 2009). So co-digestion can be employed to control inhibition of AD caused by volatile fatty acids. In literature it was analyzed the effect of co-digestion of wastewater sludge and dewatered cow dung in dry methane fermentation. Different mixtures of both of feedstock in varying ratios (1:0, 4:1, 3:2, 2:3, 1:4 and 0:1) were digested together in mesophilic temperature range in laboratory in batch setups for a span of 63 days. They concluded that for ratio 2:3 maximum biogas generation was achieved as 0.503 m³/kg VS, VS reduction of 54.80%, total organic carbon reduction of 70.71% and specific methane generation of 0.328 m³/kg VS comparing them with other ratios and mono-digestion. It was too concluded that due to co-digestion 3.11 to 3.99% more methane gas yields were generated because of synergistic effects. Diaz et al. (2014) in his study co-digestion of different waste mixtures from agro-industrial activities concluded that Synergetic affects giving improved methane yields compared to the methane potentials of the individual substrates. Pana et al. (2011), conducted AD trial to study the potential of methane production from vegetable and fruit waste. In batch reactor it is exhibited that though by keeping the pH and addition of nitrogen inside the reactor,

improved results could be taken for the production of biogas ($0.42 \text{ m}^3 / \text{kg VS}$), generation of methane (50%), and high uptake of VS from the feedstock.

Mashad et al. (2010) concluded that results of the screening cattle manure on biogas generation by dairy leftover in mesophilic (35°C) thermal environments in batch type of digestion. This research study examined the biogas generation potential by co-digestion of unscreened food waste and cattle manure and its contrast the generation of biogas when these wastes were digested alone. The outcomes clearly disclosed that generation of biogas by co-digestion of food waste and cattle manure was considerably augmented till 60% of initial volatile solids.

Budiyono et al. (2010) tested the effect of different percentages of TS in feedstock for generation of biogas at laboratory scale. The results indicated that 7.4% and 9.2% total solids in the substrate proved best efficiency in the digestion. .

Fang et al. (2011) concluded the use of potato juice, the organic by-product from potato starch dispensation, for biogas generation was examined in batch evaluate and in in elevation rate anaerobic apparatuses. The highest methane latent of the potato-juice dogged by batch assay was $470 \text{ mL-CH}_4/\text{gVS-added}$. Anaerobic digestion of potato-juice in an EGSB reactor can attain a methane yield of $380 \text{ mL-CH}_4/\text{gVS-added}$ at the OLR of $3.2 \text{ gCOD/ (L-reactor.d)}$. In UASB apparatus, advanced OLR of $5.1 \text{ gCOD/ (L-reactor.d)}$ can be accepted, though, it occasioned in an inferior methane return of $240 \text{ mL-CH}_4/\text{gVS-added}$.

2.4 Benefits of anaerobic co- digestion

Generation of methane is normally considered in environments where sewage sludge or cow dung is employed as most important resources of energy. The use of agricultural waste and sewage sludge include the conversion of less efficient fuel into better and more usable one , recovery of fertilizer that can be lost in case agriculture waste is burnt directly and may have an effect on public health (in eye and lungs) in case fewer smoke producing, cleaner biogas is used. Biogas has recognized it as renewable source of energy which hampers dependence on conventional fuels, greenhouse emissions. It can be employed in both stationary and mobile sources, if made in better bio-methane form.

Digestate obtained from AD is exceptional additive that produced extra income source for peasants concerned. In addition employing AD processes reduces odors and helps to create many jobs. The key use of agricultural waste and cattle manure is its burning directly. Anyhow it includes public health risks and ender user is exposed to pollutants. The mitigation of public health risks and efficiency is achieved by changing agricultural waste to any other useable fuel by biological and thermal processes. The consequences of variation in the form of secondary fuel sources are as ethanol, methanol, hydrogen or bio-methane. The heat obtained by these can also be used for heating, baking, cooking, for steam production that can be used to generate electricity.

As similar organic ingredients and methane yields elimination were attained in dry fermentation of cow dung by wet fermentation equally at thermophilic and mesophilic temperatures, it may be a likely alternate to the orthodox process. Additionally, no important alteration in the class of the biogas was noticed cumulative primary TS of cow dung in range of 7.68% to 15.18%. Higher total solid of the dry-digestate (10.87%) not only customs the management of the digestate at ease but too drops the need of space for composting. In comparison, wet fermentation needed higher volume of reactor and more energy to keep the temperature of reactor for similar rate of loading. (Jiang et al., 2013)

The temperature phased anaerobic digestion system working on retention time of 14 days had been operated to changing total solids amount ranges (3.46–14.54%) of wastes of dairy cattle. At TS amounts lesser than 12.20%, relating to system volatile solid loadings ranging of 1.87–5.82 g VS/L/day, the setup achieved average VS elimination of 40.2%. The extreme VS removal of 42.6% was attained at total solid amount of 10.35%. CH₄ retrieval from the wastes was consistently within 0.21–0.22 L/g VS fed. There was a drop in the system presentation related to removal of volatile solids and CH₄ retrieval at total solid amounts more to 10.35%. VFA/Alk lesser to 0.10 in the mesophilic reactor 0 and.35 in thermophilic reactor were obtained optimum for constant processing of the system. For whole series of total solid amounts, the pointer organism amounts in the bio-solids were in the ranges

stated by USEPA in 40 CFR Part 503 regulations. At completion of digestion, closely 80–85% of total phosphorus was related to bio-solids. (Ageyman et al., 2014)

2.5 Factors effecting AD process

2.5.1 pH

AD has optimum range of pH between 6.5-8. Toxicity is observed under low pH that is related to presence of volatile fatty acids accumulation. Methanogenesis slows significantly as pH lowers than 6.3 or elevates than 7.8 as it slows down generation of biogas. Lesser pH results in accumulation of filamentous microbes and high pH results in elevation of NH_3 .

In high-solids CH_4 generation through digestion of sludge, range of at 6.6-7.8 was found operational in mesophilic environments in moisture of 90- 96%. 6.8 was the optimal pH; though the progression might flop in case pH is below range 6.1-8.3. (Sosnowski et al., 2003)

Decrease in pH can be made precise through augmentation of NaOH, lime or Na_2CO_3 . It is stated in literature that and pH above 7 and alkalinity of around 2,500 mg CaCO_3/L was kept through addition of 0.2 gram of sodium hydroxide per gram VS. The conclusions of this research showed that it was essential to employ agents, like sodium hydroxide, for controlling pH in single-stage dry anaerobic reactor with food leftover. (Jiang et al., 2013)

As anaerobic degradation progresses up till the phase of methanogenesis, degradation of protein enhances NH_3 amounts by discharge of amino groups. The generated NH_3 turns as buffer material, in that period, pH can be achieved till 8 or beyond. Afterwards stabilization of methanogens, pH develops stable in range 7.2-8.2. So, in anaerobic reactor, NH_3 is too accountable for cushioning, and stabilization of pH when existing up till 1000 milli-gram per liter value. In literature it is concluded optimal pH relating to total ammonia nitrogen amount under both thermophilic and mesophilic environments. They established, the optimal pH values are near to 7 in mesophilic digestion of municipal solid waste autonomous of TAN values. Though in thermophilic environments, it is perceived 7.5 is the optimal pH when Total

Ammonia Nitrogen is more than 1,331 mg/L and that can be available in range of 7 to 8 of if total ammonia nitrogen is lower /equivalent to 1,331 mg/L.

2.5.2 Temperature

One of the important aspects involved in anaerobic digestion is temperature of anaerobic digesters. Anaerobic digesters usually work in mesophilic temperature range i.e. 30 to 40°C or in medium thermophilic range. Best results of anaerobic digestion are obtained in thermophilic range but economy of system is kept in consideration as more energy is required to achieve thermophilic range. For higher thermophilic range the system imbalances. At temperature range of 50-60°C AD is more balance and performs better than mesophilic range. When comparing to thermophilic systems, mesophilic setups too display adequate stability of process and elevated growth of bacteria, they give lower yields of methane and undergo poor biodegradability and hindrances associated to imbalance of nutrient. (Bowen et al., 2014).

Keeping in view scenario of Pakistan, we have moderate temperature and mesophilic range is achievable throughout the year. As we have energy deficiency there is an energy constraint related to thermophilic setups. Thus for Pakistan mesophilic range of anaerobic reactors is preferred. Further to it, 15-30 days are required to treat waste under mesophilic conditions this also a moderate range and can be employed. (Mao et al., 2015)

2.5.3 Solid's retention time (SRT)

The standard duration spent by solids in digester is called SRT or solid's retention time. Average duration spent by liquid sludge in digester is called HRT or hydraulic retention time HRT and SRT are same in conventional anaerobic digesters as feedstock or biomass is neither charged nor discharged/recycled. SRT has a direct link of mixing in the successive steps of digestion. For an engineer it is most important design constraint that links to growth rate of biomass or feedstock in a simulated setup constantly. For AD of municipal sludge's 15-60 days in digestion

chamber is considered ample duration depending upon temperature. The effect of temperature and SRT has been reviewed in literature

AD of sludge as well as decrease in Volatile Solid content of feedstock. It was concluded that by increasing SRT and temperature VS content is decreased to limit for SRT and is proportional to temperature. Relation of SRT and digestate stability varies from substrate to substrate (Kwietniewska et al., 2014)

2.5.4 Ammonia-nitrogen as inhibitory and toxic compounds

A number of substances can be a source of inhibition reactions like heavy metals, cations, sulfide, and ammonia and light metals. During reactions sulphates restricts methane generation by giving a substitute as an electron receiver. Sulfide causes requirement of oxygen which decreases mound of chemical oxygen demand treated. For methanogens there are many compounds of carbon which cause inhibition Toxicity by NH_3 in one of the key factors in anaerobic reactions and treatments if wastewaters including elevated amounts of $\text{NH}_3\text{-N}$ and TAN. Free NH_3 is reflected as toxic for methanogenic microorganisms. Minimum amount of ammonia that is considered as toxic for methanogenic bacteria in anaerobic digestion is 100 mg/L (Grady et al., 1999). In batch start-up phases in literature it was concluded that inhibition through Ammonia-Nitrogen complex was more pronounced when it was in range of 1500-3000 mg/l in form of Tan and pH was greater than 7.4. In literature it was reported, in mesophilic temperature environments inhibition limits of ammonia-nitrogen are about 2000 mg/l provided at pH range of 7.5 to 8.0 (Kwietniewska et al., 2014)

2.5.5 Organic loading rates

Organic loading rate (OLR) represents the quantity of feedstock added on daily basis in the digester and mostly, it is mentioned in kilograms of VS per m^3 per day ($\text{Kg VS}/\text{m}^3/\text{day}$). The gas generated on daily basis in a reactor actually rests on on its organic loading rates (OLR). Volatile solids are basis of loadings for organic sludge and solid waste. Chemical oxygen demand and biological oxygen demand are considered as loadings for dilute wastewater. Anaerobic digestion as well as gas

generation rate relies on OLR. It has been observed that AD destabilizes at higher organic loading (Jabeen et al., 2013). Gou et al. (2014), reported higher destabilization and loss in VS removal at higher OLR's for sludge.

2.5.6 Mixing

Mixing is quite significant for effective transport of organic feedstock to the microbial microorganisms and homogenization of medium present in reactor. Additionally, stirring helps to transfer of heat and so abstains difference of temperature equally in high-solids and low-solids anaerobic reactors. Likewise, it halts settling of dense material in the reactor and aids in discharging generated gas of reactor materials a quite number of procedures for stirring include recirculation of the generated biogas by pumps, recirculation of digestate, or mechanical mixers 2.5. Though, recirculating feedstock is considered as utmost appropriate method for this and comparing it with mixing mechanically and recirculation of biogas, made elevated biogas volumes from feedstock when total solid contents are higher that of 10% . Furthermore, irregular stirring has been concluded as appropriate for feedstock transformation and elevated generation of biogas. A comparison of CSTR and plug flow reactors as their effect on AD indicates appropriate mixing exhibits better performance and enhanced biogas generation as compared to plug flow systems. (Hu et al., 2013)

2.5.7 Hydraulic retention time (HRT)

Hydraulic retention time is the period spent by feedstock in reactor for anaerobic degradation. HRT rests on the thermal conditions in system. For high temperature the hydraulic retention time is less as compared to the lower temperatures. For thermophilic environment the required hydraulic retention time is about 15 to 25 day while that required mesophilic conditions ranges between 30 – 50 days (Demetrides, 2008). 3 kg/d of daily loading rate, 27 days of hydraulic residence time, 2.5 to 3.0 kg VS/m³/d of OLR is reported for sludge waste combinations (Scano et al., 2013).

2.5.8 Carbon to nitrogen ratio

Carbon to Nitrogen ratio illustrates the percentage of amount of Carbon and Nitrogen in any organic substrates. N is required by microbes for their reproduction by forming new cellular materials. Appropriate ratio of nutrients C: N: P: S for methane generation is 600:15:5:3. So, carbon to nitrogen ratio of 20 to 30 is concluded most promising that provides adequate quantity of N to make cells of microorganisms and to degrade carbon present in waste.

In AD, materials with less nitrogen do not degrade and continue to heap in reactor and cause inhibition during anaerobic digestion. Consequently, carbon to nitrogen ratio of the feedstock is quite critical constraint. Since if the carbon to nitrogen ratio is has high value, it indicates that feed is lower in nitrogen and higher in carbon material, thus low nitrogen fraction would be swiftly used from methanogenic bacteria, then the generation of biogas will be low because of lower nitrogen. Opposite to it, if carbon to nitrogen ratio of the substrate is lesser, it results into high N, which will mount up within reactor in duration that elevates pH till 8 or more and will turn into materials that are toxic to methanogenic bacteria. Lessen NH₃ amassing issue in dry thermophilic AD, carbon to nitrogen ratios range of 27-32 is referred in literature. Wang et al. (2014) referred C/N ratio as control feature for AD. It was indicated that in co-digestion substrate is used for balancing the carbon and nitrogen content of each. Effect of rice husk as low nitrogen and high carbon source was considered as effective substrate content to be added with chicken and dairy manure. Below mentioned is data indicating C: N of different materials (Dioha et al., 2013)

Table 3 Carbon to nitrogen ratio of different materials

Material	C/N Ratio	Material	C/N Ratio	Material	C/N Ratio
Alfalfa meal	15	Newspaper	400-850	Compost	15-20
Animal tankage	7	Aquatic plants	15-35	Potatoes (culled)	18
Oat straw	50-100	Paper fiber sludge	250	Corn silage	35-45
Apple pomace	48	Cardboard	560	Poultry manure	5-15
Paper	125-180	Paper pulps	90	Corn wastes	60-120
Rice husk	110-130	Sewage sludge	5-16	Paper mill sludge	55
Cottonseed meal	7	Fish wastes	2.5-5.5	Coffee grounds	20
Sawdust	200-750	Seaweed	5-27	Sawmill waste	170
Food wastes	14-16	Pig manure	10-20	Potato tops	28
Cranberry wastes	30-60	Sheep manure	13-20	Crab/Lobster wastes	4-4.5

Table 3 indicates is indicating carbon to nitrogen ratio of different materials. From this table it is shown that a combination of different materials can be used to make adequate mixture to be fed in an anaerobic digester by maintaining C: N in range of

25-32. It is evident from above table 3 that a mixture of rice husk and sewage sludge had an ability to be used as a substrate in conducted study.

2.5.9 TS content

Total solid content is an important parameter in anaerobic digestion. Type of anaerobic digestion is based on its total solid content. For dry anaerobic digestion total solid content is kept in limit of 15-40% and for wet anaerobic digestion it is < 15%. Reactor volumes and fluid ability of substrate is based on its total solid content. The total solid range in dry digestion limits the size of reactor and a variety of feedstocks are acceptable when dry digestion is employed in AD. (Yi et al., 2014)

2.6 Design of reactor for anaerobic digestion

Fundamental needs of an AD reactor designing are to allocate for a semi-continuous higher and workable rates of organic load, an optimum time of hydraulic retention, to have the supreme yield of methane. The kind of reactor is too quite significant in generation of biogas (Shen et al., 2013). There are 3 main types of digesters designed on operation mode for anaerobic digestion that are one stage continuous, batch and multistage continuous and are being discussed below.

2.6.1 Single-stage batch systems

Digesters under batch mode once added with substrate, inoculum to start the digestion process and in some cases some chemicals are also added for the buffering of pH changes. After that the digesters closed air tight and the process of anaerobic digestion is allowed to start (Nijaguna, 2002). In batch digestion form the digesters are packed once for anaerobic digestion and when the process is done the whole feedstock material is taken out from the digester. The gas production gradually builds up and after some time reaches to its highest point and then the decline in the gas production starts, creating a bell shape curve (Nijaguna, 2002). This method supports simple administration of the waste material but the difference in the production of gas is more both quantity and quality wise. Therefore different digesters are functioned simultaneously giving a gap of a few days to avoid any disruption in production and

consumption of gas. This method also provides high degradation of feedstock if the time of the digestion is enhanced (Demetriades et al., 2008).

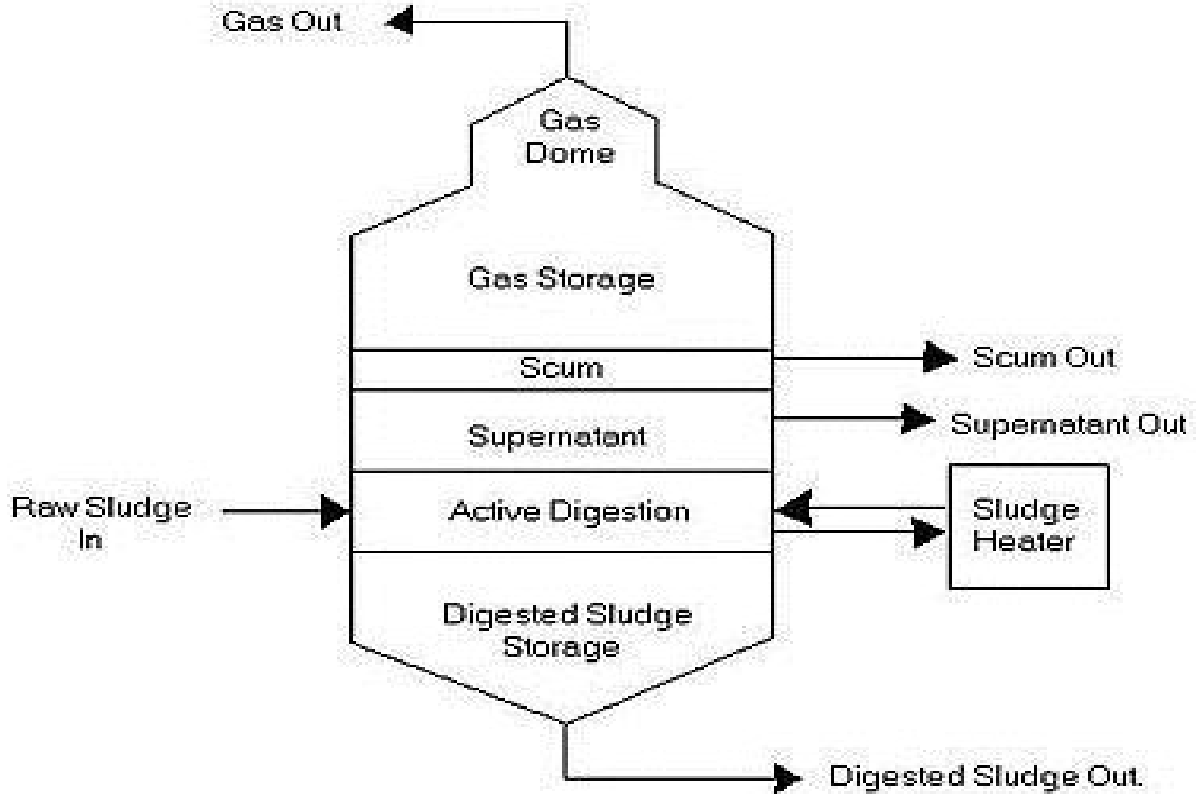


Figure 1 Single stage anaerobic reactor

2.6.2 Single-stage continuous systems

For continuous digesters, feed is charged and discharged of digester on continuous basis. The feed is continuously charged all of the biochemical reactions related to production of biogas take place in nearly constant rate. The setup is charged with said weight gradually with passage of time occurs on continuous basis with no endpoint. A reasonably consistent rate for biogas generation is outcome of this. In Europe full scale single-stage continuous setups comprise over 87% of total digestion ability of sewage sludge and bio waste (Demetriades et al., 2008). Industry related people give preference to such digestion setups as they have simple designs and investment cost on them is also low comparatively. Such setups require lower area and its service cost is also low. Prominently high initial expenditure can be compensated by cost reduction of

real state in places where area of land is rare. Anyhow, a technical and engineering issues related to pumps are faced in feeding the substrate when it is done on continuous basis. Homogenization is one of the key concern of all setups involving AD as such setups depend on pumping to have their smooth function. Also such setups demand higher fluid flow while charging and discharging substrate (De Baere, 2006).

Figure 1 is a schematic diagram of single stage anaerobic reactor. It illustrates the mechanism of raw sludge input, gas outlet and digestate medium outlets. Sludge heating is provided by external heating mechanism by any method that could be a water bath, hot water circulation or electric stove. A free board just below biogas outlet is the free board left for accumulation of biogas.

These setups are thus suitable in digestion of low solids feedstock. For high solid feeds, handling and transport of feed is done by use of powerful pumps, screw and conveyer belts that are especially made for denser feeds. This sort of equipment is quite costly. There is variation of studies in such setups. These setups are charged at continuous gaps as an example daily or on small gaps with corresponding discharge of feed. Biogas generated in these setups is more constant and has uniform characteristics. Elevated generation rate referred to feed that is present in its real form and its density is not decreased by water addition. The variation in continuous and semi-continuous systems is subjective. Much of continuous setups at higher scales are not continuous totally. Those function in semi continuous phase. The definition of continuous setups is employed in larger scale that compromises only to semi-continuous or continuous digesters that are charged or discharged only one or two times daily. (Lissens et al., 2001)

2.6.3 Multi-stage continuous systems

We know there are 4 phases when anaerobic digestion takes place. By figure 2 it is shown as each of these phases constant action of separate digesters is usually achieved in two-stage digestion setups. In the initial setup, hydrolysis and acetogenesis occurs whereas in the second digesters, methanogenesis is achieved. The restraint in initial digester is cellulose's hydrolysis rate while growth of microorganisms is the constraint for second setup. By distributing the reactor into two parts, this permits improved governance on rate of hydrolysis and methanogenesis. By above figure 2, it is shown that biogas can be collected from the top of both reactors as outlets are provided, while scum and supernatant removal outlets are provided in 2nd reactor. Outlet for stabilized sludge is provided in 2nd

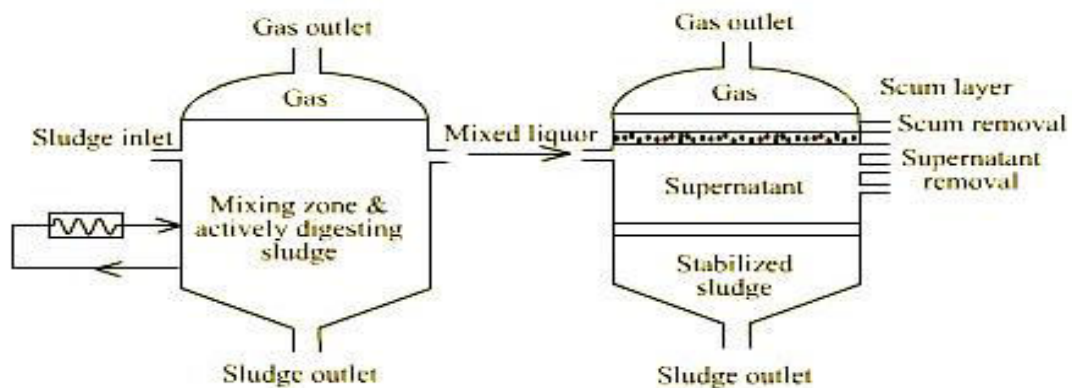


Figure 2 Multi-stage anaerobic digestors

reactor. One of the benefits of this system is that we can use the digesters as storage devices. Furthermore, for speedily degradable waste materials (sludge, food waste, etc.), an elevated natural stability is achieved (O'Keefe and Chynoweth, 2000). So in multi stage setups have better VS reduction and they were presented by research community administer and inspect transitional phases during anaerobic digestion. So in continuous state of anaerobic setups classification can be classified on basis of single and multi-stage setups.

Constant action of 2 setups is normally done in 2 stage setups. In 1st setup hydrolysis takes place along with acetogenesis. In the other reactor methanogenesis takes place.

Hydrolysis rate of cellulose is restrained in first reactor and growth of microbes is restricted in 2nd stage. When we distribute the setup in 2 stages it permits more control over rate of hydrolysis and occurrence of methanogenesis. In such setups, we employ various mechanisms to enhance reaction rates. Like hydrolysis reaction rate can be augmented through micro aerobic situation. Another of the benefits of this setup is storage devices can be made through reactors. Further to this for efficient digestion of substrate an elevated natural stability can be achieved.

2.6.4 Continuous digestion

In continuous anaerobic digestion the feedstock, material is charged and discharged through a digester about 1 to 8 times per day (Demetriades, 2008). In this process the new feedstock added thrusts same volume mature feedstock material through the digester whose hydraulic retention time is nearly finished, thus keeping the persistent volume in the digester. Such type of digestion keeps a reliable and stable production of biogas, in comparison to batch digestion, because of continuous feeding of material to the digester (Demetriades, 2008).

2.7 Types of solid wastes for anaerobic digestion

2.7.1 Lignocellulose comprising waste

Lignocellulose comprising feedstock mostly contains agriculture and logging leftovers with crop remains forming the common. In China, nearly 800 metric million tons of leftover agricultural straw is generated annually. This leftover is not digested intrinsically because of intractable constituents (cellulose, hemicellulose and lignin,) which results in little biodegradation and reduced performance of digestion; so, more incremental procedures are required to initiate process of digestion like inoculums and pre-treatment. For inoculum, enzyme behavior leads in elevated substrate deprivation and generation of biogas (Gu et al., 2014). One more trait of inoculum is nutrient stuffing that boosts the generation of biogas and activity of enzyme. Anyhow, lignocellulose waste has a high carbon to nitrogen ratio that results in decline biogas generation; so co-digestion of other organic matter wastes and comprising lignocellulose and is frequently suggested. Preceding researches concerted on anaerobic digestion of agriculture straws and shared this developments

along with numerous pre-treatments are required to the leading anaerobic digestion progression, circumstances of digestion mainly drawn in co-digestion along with other solitary batch-digesters mesophilic, and organic matter.

2.7.2 Municipal solid waste

With improvement of economic conditions resulted from rapid industrialization large metropolitan cities have risen. As a consequence of life so much waste is generated and ultimately resulting in to issue of municipal waste management. Municipal waste management includes in its collection, storage and ultimate disposal. In recent times municipal solid waste is employed to transform it into energy by use of technology. Anaerobic digestion has a key role for processing of municipal solid waste and generation of energy (Hadj et al., 2009). Key benefit of AD is smaller values of digesters and low use of energy and water. Anyhow slow anaerobic digestion operations, various high technological equipment and generation of toxic compounds in digestion are major drawbacks. Employing municipal solid waste in anaerobic digestion is a solution to counter problems related to management of solid waste as well as it will help to generate energy out of it (Fernández-Rodríguez J et al., 2014).

2.7.3 Livestock manure

Now a day in many countries concentrated farming of livestock is progressing. One of the associated features is management of waste related to it. Plenty of cattle dung increases its requirement to convert it as fertilizer and thus minimizing its harmful impacts on human life and environment. AD of this waste is not feasible alone because of nutrient inequity and inhibition caused by ammonia. Generally cattle dung has large amounts of nitrogen as swine manure (0.24%), dairy manure (0.35%), chicken manure (1.03%) and fresh goat manure (1.01%). Cattle dung has ability to level carbon to nitrogen of single straw leftovers. And adjustment of pH is also done by ammonia formation. Thus using any other material with adequate high carbon to nitrogen ratio and low pH can be used alongside cattle dung for adequate anaerobic digestion. (Li et al 2014, Yin et al., 2014)

2.7.4 Waste activated sludge

In addition to the organic feed discussed previously, waste activated sludge (WAS) is one more sort of reserve for anaerobic digestion procedure (Evan, 2005). Due to growing industrialization, amount of waste activated sludge is increasing quickly. Cellulose and protein are the two key constituents of such kind of sludge, that biodegrades to generate biogas. Normally, the process of anaerobic digestion of waste activated sludge (WAS) comprises of 3 phases:

- Hydrolysis of biological compounds,
- Transformation of hydro-lysates to hydrogen and acetate
- Conversion of acetate and hydrogen into methane.

Similar to other anaerobic digestion processes the rate-limiting step in the AD of WAS, is hydrolysis but can be prevailing over by enhanced amounts. Additionally, WAS displays fairly little degradation, mainly at long sludge retention times. So, to speed up digestion of sludge, diverse pre-treatment methods are implemented in recent times, that include alkali treatments, thermal hydrolysis, biological (mostly thermal phased anaerobic), mechanical (such as ultrasound, high pressure and lysis), (mainly ozonation chemical with oxidation), and other co-treatment methods. Intention of biological pre-treatment is enhancement of hydrolysis prior to major digestion process. Application of thermal hydrolysis helps to achieve partial digestion of sludge through improvement of dewatering ability. As per preceding studies, most encouraging range of temperature is 160–180 °C with dispensation times of 30–60 min. Though, another research has showed that treatments at elevated temperatures (170–190 °C) consequence in little sludge biodegradability in spite of high digestion proficiencies. Mechanical treatment approaches concentrate on provision of reasonable performance progresses along with reasonable electrical input. (Borowski et al., 2014)

2.8 Hydrocarbon generation of anaerobic sludge

The feature of raw sludge heating values of sludge if compared with wood, have similarities. Secondly accumulated or gathered sludge had lesser heating values. It

can be attributed to release of CO_2 and C_nH_n release as a result of stabilization. For the time being, sludge generated by AD of sludge being used as inoculum and waste had reasonably elevated amounts of hydrogen, oxygen and carbon when it was compared with stabilized sludge. So for thermal alteration of bio-fuels anaerobic sludge is a better alternative, owing to its higher heating value a number of studies have referred that temperature is a limit when biomass is conversion. So optimization of temperature of pyrolysis is essential to enhance gas yields and bio-oil .A methodical assessment of transformation of biomass at varying temperatures can provide a whole scenario that how generation of biogas reacts with variation in temperature. Not only amount if biogas but its quality also shows variation with change of temperature.

2.9 Techniques for enhancing generation of biogas

Biogas through AD of organic materials is an energy resource that is renewable that contains mostly of CO_2 and CH_4 . Minute constituents which are normally obtained in biogas are hydrogen sulfide, water vapor hydrocarbons, siloxanes, ammonia, oxygen, nitrogen, and carbon monoxide. Seeing the biogas as a renewable and clean form of energy that might well standby the conservative energy source (remnant fuels), the adaption of such form of energy develops significant. Numerous optimization methods in biogas generation process had been established, comprising, biotechnological approaches pretreatment, co-digestion as well as the use of sequential digester. For roughly application, the definite purity of biogas is desired. The occurrence of carbon dioxide and other trace constituents in biogas might disturb required performance adversely. Decreasing CO_2 content will considerably improvement quality of biogas and increased calorific value. Biogas can be cleansed from carbon dioxide by means of pressure swing adsorption, physical or chemical CO_2 absorption membrane separation (Andrani et al., 2013, Tippayawong et al., 2010).

Solid particles of feedstock are crushed into very small pieces through mechanical pre-treatment. That aids to enhance surface area of feed that gives improved contact of feedstock and microbes and ultimately enhance biogas are generated. Feedstock

consumption rate and surface area of particle are inversely related to each other i.e. smaller the size of particle more surface area and more the biogas generation rate. The reactors face problem of clogging when particle size is high (Agyeman et al., 2014).

Dewatering of feedstock, removal of pathogen, decline in viscosity is achieved by thermal pretreatment. Moreover, thermal pretreatment dismantles the membrane of cells and increases homogenization of organic matter.

On lesser temperatures (lesser than 100° C) composite materials do not degrade. An increase from 7.9 to 11.7% was experienced in generation of biogas when temperature employed for pretreatment of feed stock comprising of fruit and vegetable waste was 175° C (Liu et al., 2012). Anyhow 24% higher biogas generation was recorded in literature when employed temperature was 120° C.

Chemical pretreatment assists in disintegration of structure of organic matter. Major chemical used for this purpose are acidic or strong alkaline materials. They too like thermal pretreatment methods, degrade lignin content of biomass. An effect of toxicity abatement is also observed by chemical pretreatment.

Few other ways of enhancing the efficiency of anaerobic digestion i.e. methane generation is bio-augmentation that enhances activity of intrinsic microbes.

Legumes and some plant leaves are used in a form of additives that resulted in enhancement of biogas production

Ultrasonic pre-treatment of waste activated sludge for 30 minutes gave boost up till 64% as reported (Wang et al., 2014).

2.10 Environmental benefits of anaerobic digestion

6.1 Gt CO₂-eq/year and 5.1 Gt CO₂-eq/year of greenhouse gases were contributed by agriculture sector in year 2005. This in around 10-12% of total GHG Emissions in that particular tenure.

These agriculture segment sources of GHG emissions comprise rice grown, use of manure in agriculture fields, and storage of cow manure. The main gases from them contain nitrous emissions and methane (CH₄). Nitrous emissions are mostly

generated as a consequence of the anaerobic and aerobic activities in the storage areas of cow manure. Contrary, the treated/digested slurry decreases emissions of NO_2 . Between the treatment approaches of cow manure, composting decreases 30% emissions and nitrous oxide production is declined 28% through anaerobic digestion. Diverting food wastes of landfills and to developed technologies will stop these wastes and GHG release whereas at the similar time create a source renewable energy by complying the emitted gases (Matthew Franchett, 2013).

2.11 Studies on production of biogas from sludge

Alqaralleh et al. (2016) in his study of thermophilic and hyper-thermophilic co-digestion of waste activated sludge and fat, oil and grease concluded 112.7% more methane has been achieved using hyper-thermophilic co-digestion of TWAS-FOG. Razaviarani et al. (2013) in their study of pilot-scale anaerobic co-digestion of municipal wastewater sludge with restaurant grease trap waste concluded that Mesophilic co-digestion of MWS and GTW was found to be feasible up to a maximum GTW amounting to 23% of the 1.58 ($\text{kg VS/ m}^3/\text{d}$). Silvestre et al. (2014) in his study of thermophilic anaerobic co-digestion of sewage sludge with grease waste concluded that As OLR values increased from 2.2 to 2.4 and 2.8 $\text{kg COD/m}^3/\text{d}$, the methane increased 1.2 and 2.2 times.

Kuglarz et al. (2013) concluded that the sludge was pre-treated by low-temperature thermal and microwave irradiation method, both piloted under the same temperature range (30–100 °C). Microwave pre-treatment was establish to be superior over the thermal treatment with reverence to sludge solubilization and biogas generation. Taking into description the specific energy demand of solubilization, the sludge pre-treated at 60–70 °C by microwaves of 900 W was selected for additional trials in unceasing method, which was more actively workable related to lower value (700 W) and thermal management. Continuous biogas container trials showed that pre-treated sludge (microwave radiation: 900 W, temperature: 60–70 °C) gave 35% additional methane, related to raw sludge. Furthermore, the consequences of this study obviously confirmed that microwave pretreated sludge presented improved mark of cleanliness.

Co-digestion is a method of coalescing numerous feedstock constituents in same AD setup to enhance total methane concentration. During previous few eras, miscellaneous organic feeds are been considered which indicated synergistic effects of the mutual treatment. The co-substrates usually comprise, organic solid waste), cotton wastes (sewage sludge micro-algae and rice stalks (Esposito et al., 2012).

2.12 Sludge management options

Sludge of sewage is derivative of municipal wastewater treatment process; though, sludge treatment problems are frequently ignored in contrast to water-relating limitations like the departing load and the grade of elimination of varying wastewater complexes. Sludge is a possible hazard for the surroundings; for example, bubbling sludge can misplaced through treatment or sewage sludge can be even intentionally discharged of into waterways.

The applied and practical trials of sludge management are:

- stabilizing – sludge is not inactive and can has an nasty smell;
- decreasing the water content and volume to least;
- using the energy potential when lavishly probable;
- decreasing the sum of dangerous microbes if animals, people or flora are in interaction with sludge
- Retrieving phosphorus for cultivation.

Treatment of sewage sludge is much additional to only digestion, thickening, and disposal and dewatering. It has significance for entire treatment setup:

- With sludge-generated biogas, it is thinkable to enhance energy generation (thermal and electrical) more than 100% of power required in plant. Energy generation and energy efficiency are thus very significant subjects. It is also possible to increase biogas production with certain pre-treatment methods.
- During AD nitrogen is compacted to NH_3 that has elevated amount in the discard water which is disjointed from sludge while dewatering. Improved digestion affects a greater reject load of water.

2.12.1 Sludge thickening

The sludge which is produced from wastewater treatment has water percentage among 99.5 % and 97 %. In thickening of sludge, dry solids content in sludge is enhanced by decreasing water content through little input of energy.

Thickening extra sludge has more significance since after secondary sedimentation; the dry solid content of the sludge is around 0.5–1.0 %, whereas main sludge from PST can have a dry solid percentage of up to 4.0 %.

2.12.2 Sludge dewatering

The sludge dewatering procedure is comparatively simple: enhancing the DS percentage of the sludge with diverse types of apparatus. This unit procedure constantly needs the usage of in any case some flocculent assistance which retains the extra sludge flocculated in unit of dewatering. Occasionally, coagulation chemicals like aluminium or iron salts are too mixed for increasing efficiency of flocculants assistances (polymers) and to decrease the usage of them in dewatering of sludge.

2.12.3 Sludge drying

Thermal drying is an innovation which targets significantly to decrease water concentrations of sludge. Drying is typically done in big wastewater treatment setups to enhance the calorific value of sewage sludge in incineration. Also, drying is not often practised because of its high costs for agricultural disposal. The elimination of water through evaporation by treated and dewatered sludge enhances the dry solids content in sludge, and decreases both sludge weight and volume. Sludge drying is useful for dewatered (20–30 %) excess and/or primary sludges also digested sludge later dewatering. Because of the high investment prices, it is typically limited to big setups.

2.12.4 Stabilization

The purpose of stabilisation is to decrease chemical and biological reactions to minimum. Anaerobic digestion is oldest and maximum frequently used procedures for stabilization of sludge. The first of the AD boilers were presented over a hundred years before in US. Focused inorganic and organic sludge substance is decayed by

microbes in lack of oxygen and is converted into CH₄ and inorganic products. The main advantages after digestion are stabilization of wastewater sludge, biogas production and volume reduction. The AD procedure is functioned either in the mesophilic (around 35–40 °C) or thermophilic (53–57 °C) temperature series. Thermophilic temperature is widely verified by wastewater sludges from municipal wastewaters in pilot and laboratory, full scale for last 30 years – regrettably deprived of any achievement. Its chief rewards are good procedure constancy and supernatant quality with dependable process skill. It is likely to decrease the volume of sludge significantly and have biogas for supply of energy. It is to be taken into explanation that digestion creates an important quantity of castoff water that upsurges the nitrogen and COD heaps in the wastewater treatment setups.

2.13 Methane generation process in AD

By figure 3 it is shown that three clusters of bacteria viz. acetogens, methanogens and acidogens are concerned in anaerobic biological process and complex relations of every species are related in accomplishment of process. AD is usually measured in

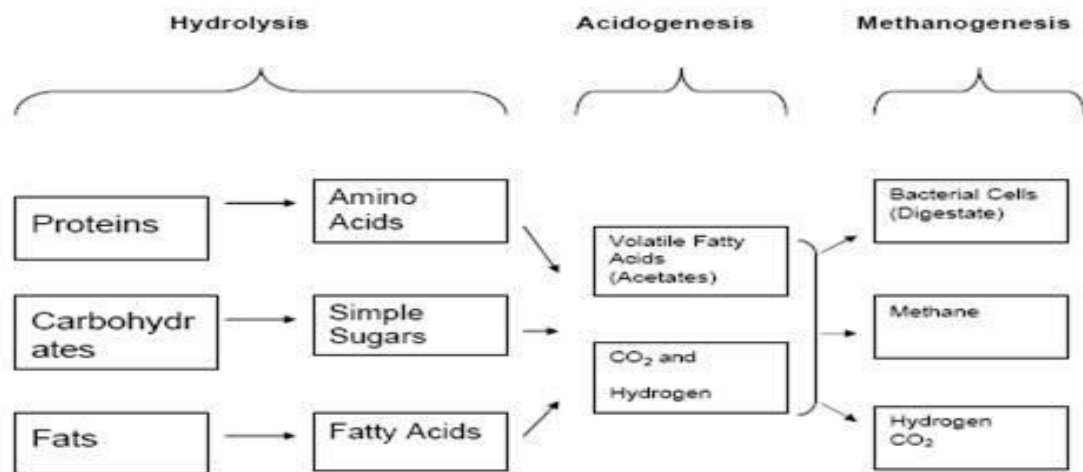


Figure 3 Mechanism of anaerobic digestion process

four consecutive stages and biological anaerobic processes; hydrolysis, acidogenesis, acetogenesis, methanogens. Figure 3 details the steps that are involved in biogas formation. Proteins are initially converted in VFA, CO₂ and hydrogen likewise

carbohydrates and fats during hydrolysis. After acidogenesis the products of hydrolysis are converted into product of methane and by-products of methane and digestate, hydrogen gas and carbon dioxide.

This involves waste variation and stabilization (Jarvis, 2004). The finish materials are mainly methane, stable organic residues and carbon dioxide. These progressions are further elaborated in figure 1.

2.13.1 Disintegration

The first phase included in AD is disintegration. During this phase, the anaerobic degradation of particulates and compounds (i.e. colloidal 10 - 1000 nm or bigger particles > 1000 nm) occurs largely by physically trims and disbanding whereas few extracellular enzymes can too be included (Kommedal, 2010). Complex organic materials disintegrate in their basic products; carbohydrates, proteins, inerts and lipids.

2.13.2 Hydrolysis

This phase in hydrolysis includes transformation aided by enzyme of unsolvable organic compounds which has higher molecular mass, like carbohydrate, lipids, proteins, and fats etc., in solvable organic constituents like, monosaccharide fatty acids, amino acids, and range of additional simple organic complexes. The bigger particles which are not soluble comprise quite a few smaller molecules joined by each of them in a closely packed chemical bond thus it should be whipped up before entering into cell of bacteria. Numerous anaerobic and facultative bacteria perform the hydrolysis (Yadvika et al., 2004).

2.13.3 Acidogenesis

Acidogenesis is 2nd stage of anaerobic digestion in which acidogenic microbes additionally breakdown substrate products later hydrolysis. These fermentative bacteria generate an acidic environment in the reactor with forming, H₂, ammonia, H₂S, CO₂, carbonic acids, shorter volatile fatty acids, alcohols and small quantities of other byproducts. As acidogenic microorganisms additionally breakdown the organic

matter, it is still too big and unfeasible for of methane generation, thus substrate should undergo acetogenesis. Acidogenesis is the quickest altering step in the growth rate of fermenters and anaerobic food chain

2.13.4 Acetogenesis

After completion of acidogenesis, short chain fatty acids are more disintegrated by number of facultative anaerobic bacteria during fermentation. CO₂, H₂, organic sulphur compounds, organic nitrogen compounds, other organic acids and alcohols are the resulted products of process of fermentation. This occurrence is called acetogenesis. At this point generation of acetic acid is significant step because this is the main organic acid that is feed for methane creating microbes (Gerardi, 2003).

In this phase, the products which were generated apart from acetic acid during fermentation during acidogenic stage which are more converted to CH₃COOH, H₂ and CO₂ in multiplicity of anaerobic oxidation reactions assisted by acetogenic microorganisms. (Jarvis, 2004).

2.13.5 Methanogenesis

In anaerobic digestion of organic matter methanogenesis is the last step in which organic matter is converted into CO₂ and CH₄. During this stage, products formed by acetogenic microbes are consumed by methanogenic bacteria that decline carbon dioxide consuming H₂ into CH₄. It is merely in this phase, incoming chemical oxygen demand is transformed to a gaseous state. (Henze, 2008). Methanogenic bacteria degrade merely few specific feedstock like formate, methylamines, methanol, acetate, and H₂/CO₂ or CO. Mixes like organic nitrogen, alcohols; etc. which remain and are not changed by methanogenic bacteria are gathered in digestate material (Gerardi, 2003, Dawood et al., 2011).

CHAPTER 3

Materials and Methods

In this chapter, methodology of anaerobic digester operation for high solids AD of sewage sludge's mixture with rice husk at multiple organic loadings, analysis of operational parameters of feed, inoculum, digestate and biogas will also be discussed.

Methodology for experimental work is sketched in figure 4

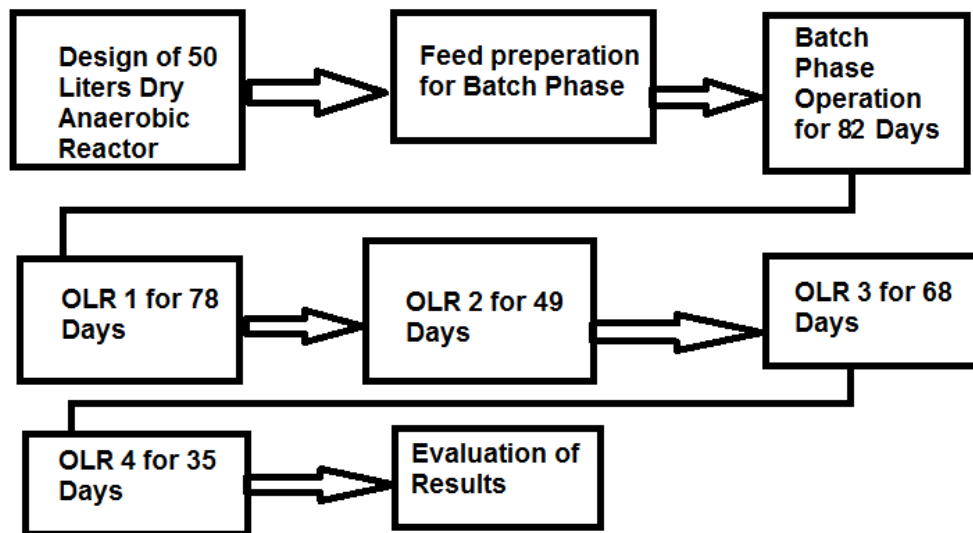


Figure 4 Methodology of experimental work carried out during the operation

By figure 4 it is illustrated that initially a reactor of 50 liters was designed. After it feed for batch phase was prepared and reactor is operated for 82 days. After it is operated at 4 OLR's of 2, 4, 6 and 8 kg VS/m³.d. After it the obtained results were evaluated.

3.1 Substrates and inoculum used in research

Below mentioned are the details of the employed materials and mechanisms for carrying out dry anaerobic digestion of waste sludge and rice husk in a pilot scale anaerobic reactor in batch start-up phase and semi-continuous phase.

3.1.1 Feed components

Sewage sludge employed in this experiment was obtained by MBR treatment plant of NUST H-12 Campus, Islamabad. Ultimate disposal of this sludge is open dumping in our country even it has high potential of energy. Fresh cow dung was taken from a cattle farm near NUST H-12 Campus, Islamabad. Digestate was collected from a Biogas Plant near Bara Kahu. Sewage sludge mixture along with rice husk in powdered form was used as a substrate. The designed ratio of feed was 60:40. Its total solid content was adjusted to 15% and 20 kg of it was taken.

3.1.2 Feed preparation

Cow dung and digestate was used as an inoculum source. After collection of waste, it was weighed by a physical weighing balance. Weight of cow dung used for the batch digestion was 6.5 kg, weight of digestate obtained from reactor was 13.5 kg and that of sludge used was 20 kg and for batch digestion. Cow dung and sludge were then mixed properly at I: S (1:1 inoculum to substrate ratio in kilogram Volatile Solids) of $1.512+0.888/2.4$ and loaded into the reactor for the batch mode.

Sewage sludge having total solids >15% was mixed with cow dung and digestate of previous reactor having total solids >0.18 and total solids >28% in ratio I: S (inoculum to substrate ratio in kilogram volatile solids) of $1.512+0.888/2.4$. The total weight of cow dung and digestate (used as Inoculums) for the batch digestion was 6.5 kg 13.5 and that of substrate used was 20 kg. Substrate, cow dung and digestate obtained from a running reactor were mixed appropriately to make homogenized mixture.

The projected values for carbon: nitrogen ratio in feedstock employed in study was derivative of literature review. No practical was carried out. The values of nitrogen and carbon were attained by final analysis in literature were employed in measurements for approximating carbon to nitrogen ratio in study. For all the three feedstock, the carbon: nitrogen ratio is supposed to be suitable for AD. Carbon content of high solids sewage sludge was measured to be 26.26% and that of cow dung was 32.36%. The appropriate carbon to nitrogen ratio for AD process lasts for 28-30. We adjusted C/N ratio at 29 as derived from the literature review.

3.2 Experimental setup

By figure 5 a sludge drying bed is shown which was designed to dewater the low solids sludge to enhance its total solids TS up to %. 3 sand filters were made which had 70 L volume containing an overhead space of 5 liters. 5 liters was filled up by uneven grains at bottom, 5L with gravel in the middle with size lesser than coarse grains and 5 liter was occupied with sand on top. Over sand, 5 Liters head space was kept empty to dewater sludge.

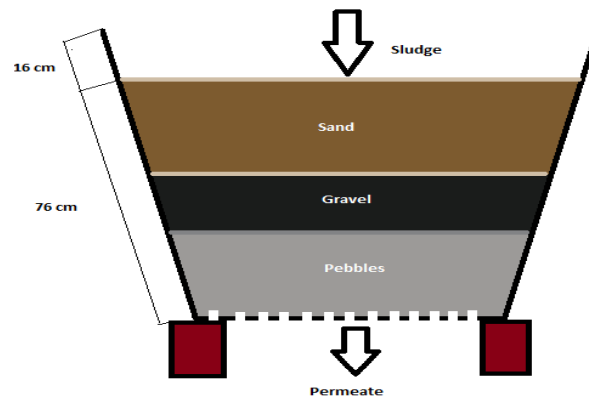


Figure 5 Sand -filter constructed for dewatering purposes

Sewage sludge was put in available head space and permitted to dry for 1 or 2 days. Water of the sludge was drained and solid sludge formed of a cake. It was then picked from top. Enhanced total solids sludge i.e. =15% was obtained.

50 liter reactor was designed for the purpose of research execution and completion. It was constructed at PetroServices GmbH-Pakistan Branch yard , under supervision of subject student Mr. Ahmad Talal who had been guided by research supervisor Dr. Zeshan Sheikh.

So the 50L reactor was designed in such a way that it had cylindrical shape and a surrounding water bath to assist heating through immersion heater. The radii of the setup 'R' was actually the height of the reactor as it was attached in a lateral position to the water-bath. Radius of setup was kept 30cm whereas optimum length was found by using the formula:

$$V = \pi r^2 l$$

$$V = 50 \text{ L}$$

$$d = 30 \text{ cm}$$

$$r = 15 \text{ cm}$$

$$\text{Hence } L = 70 \text{ cm}$$

Permanent connection of water was provided to reactor for keeping water level constant in water bath that was controlled through float valve. Whenever the water level dropped, the water started continuously flowing in bath, through water connection. These valves were present on outlet side of reactor. A drainage valve was also provided for emptying water from the bath.

Reactor was kept at angle of 25° to avoid any hindrance of digestate flow. It also aided mixing of fresh feed and digestate on daily basis. This was achieved by welding medium steel stands of 31cm and 16cm under inlet and outlet corners respectively.

To avoid heat loss and to retain the temperature, two methods were applied. Top cover of water bath was made in such a way that it had rectangular openings only at positions of Inlet, temperature sensor inlet and gas outlets, further whole of the reactor was covered with foam material to avoid any escape of heat from it.

Electronic setup was integrated in a metal box on inlet side of reactor. This mechanism was adopted to avoid any loosening of wires or avoid tripping and mingling of wires.

Mechanism include a relay switch functioned on the basis of variable temperature controller which was taking input from temperature sensor inserted in feed.

Temperature of feed was maintained at 37° C via heating rod which was heating water present in water bath. Comparative to previous run, it was fixed via ring socket near the bottom of water bath on inlet side.

The digester was constructed in a way that highly anaerobic environments prevailed in it. The cover of the tank was strongly closed and airtight properly by the use of a gas kit. Further to reactor body was welded with MS Welding Rods from both inside and outside.

A PPR inlet valve was mounted in a vertical position to assist feeding of the setup. A ball valve was connected on inlet to elude air entrance in vessel. Diameter of inlet was kept to be 0.08m in order to guarantee easy flow of feed in reactor throughout the feeding. PPR material is used in reactor to for 2 purposes i.e. economics as well as lightness of weight. Further to that a funnel of 1.5' diameter was fixed over the valve to facilitate feeding substrate.

Two gas outlets were provided in reactor to collect the biogas generated. Both gas outlets were made functional by connecting it with a wet tip biogas meter through connector. The position of both outlets was set as one near inlet and one near outlet. At times only one valve was used and other is kept spare.

A thermocouple inserting valve was also made for the providing signal of the temperature from the reactor. The thermocouple was connected to the display and relay of a temperature controller which was in turn connected to an immersion rod for temperature maintenance within the reactor.

In an anaerobic process, different groups of microorganisms are involved. The activity or inactivity of one group of bacteria affects the activity of other group. This makes anaerobic processes sensitive to inhibition due to the chemicals existing in the wastewater or substances generated as intermediates of the process. Inhibitory materials are those materials which cause a drastic shift of population of microbes or inhibition of growth of bacteria. A drop of the steady-state rate of CH₄ generation and buildup in organic acids can be taken as an indicator of inhibition (Polprasert, 2007). The maximum specific growth rate of microorganisms is reduced by inhibition which results in increment in solids retention time of a biochemical process to maintain the

same quality of effluent prior to the inhibition. Nevertheless, if the inhibitor concentration enhances sufficiently, toxic effects can be seen. It can cause total process failure due to the death of microorganisms. Generally, inhibition leads to toxicity as amount of compound is enhanced. Several inorganic materials like light metal cations; ammonia, sulphide etc. can also cause an inhibitory response except the organic materials.

For control of temperature, the reactor was placed in water bath which was packed with water; a 1000 W power electric immersion heater and thermostat was employed to keep the temperature 35° C. A relay and a temperature sensor (thermocouple) were employed to keep temperature inside the digester at 35° C.

Reactor outlet diameter was kept to be 0.08m and anaerobic conditions were maintained as the contents were fully filled up to the outlet. The digestate for analysis was collected each day through the outlet during semi-continuous phase.

3.3 Experimental conditions and procedures

After design of pilot scale dry anaerobic reactor, it is operated in two conditions initially in batch start-up phase for 87 days. No feed was added or removed during this phase except for analysis. After completion of batch start-up phase reactor was operated for semi-continuous phase for 232 days at 4 organic loading rates ranging from 2 to 8 kg VS/m³ /d.

The next section will elaborate the details of experimental conditions during batch start-up phase and semi-continuous phase.

3.3.1 Start-up conditions of anaerobic reactor.

Startup of the reactor was performed through batch loading of the prepared feed in it manually. Parameters comprising, volatile solids total solids, pH and total carbon of inoculum and substrate mixture were analyzed prior to startup and then after start-up phase on periodic basis. Reactor was operated for 87 days.

Following table shows the initial characteristics of substrate and Inoculum in batch start-up phase. Solid's retention time (SRT) is the average duration that feed spends in the reactor for digestion.

Table 4 Characteristics of substrate and inoculum

Parameters	Rice Husk	Sludge	Substrate	Cow Dung	Digestate from previous Setup (Inoculum)	Mixture of Substrate + Cow Dung + Digestate from previous Setup
Total Solids T.S (%)	56	36	15	18	28	26
Volatile Solids V.S (% of T.S)	28	68	80	75	40	43
pH	12	06	11	9	5	7
Moisture Content M.C (%)	44	64	85	82	72	74
Carbon Content C (%)	36	29	20	24	38	36

Table 4 is indicating multiple parameters maintained in design of substrate and inoculum during batch start-up phase. Total solid, volatile solids and pH were measured in laboratory whereas moisture and carbon content were measured empirically. Table 4 is indicating adjusted TS content of substrate i.e. 15% adjusted by addition of water. Solid's retention time is associated to volume of reactor and feedstock volume fed daily. For batch phase trial, solid's retention time was 82 days in mesophilic environment. Nutrients are necessary components for biomass build up in an anaerobic process like all other biochemical operations. On the other hand, nutrient requirements are less in the anaerobic processes than aerobic processes due to lower biomass yields in such processes. The C: N: P requirement ratio for a typical activated sludge process is 100:5:1 on a mass basis.

Table 5 Operational conditions during batch start-up phase

Mode	Batch Phase
Operation Time	87 days
Temperature	(Mesophilic conditions) 37°C
Recirculation Rate	15% of total substrate/day
Working Volume	40 L
Substrate Composition	Sludge & rice husk
Inoculum Composition	Cow dung and digestate
Substrate: Inoculum	1:1

Table 5 gives details of operational conditions during batch start-up phase. These conditions were maintained throughout the batch start-up phase and monitored accordingly. Recirculation rate maintained at 15% of total reactor volume. At this recirculation rate whole reactor contents were recirculate in one week. It is maintained during batch start-up phase that no reactor content is lost during batch start-up phase except for analysis. Substrate composed of sludge and rice husk whereas inoculum composed of cow dung and digestate obtained from a reactor that was already in operation. The sludge to inoculum ratio obtained was 1:1.

This is done to maintain reactor working volume as well as to ensure complete conversion of VS into biogas.

3.3.2 Semi-continuous operation phase of anaerobic digestion

After the initiation of batch mode, biogas generation enhanced with time. The rate varied with the passage of time due to unstable conditions, laterally after 86 days after stability of reactor caused decline in biogas production which was a clear indication that the organic matter present in substrate was consumed. Then the semi-continuous phase started with sludge feeding as a substrate.

Table 6 Operational conditions during semi-continuous phase

S _{no}	OLR (kg VS/m ³ /d)	Operation Time (Days)	Retention Time (Days)	Temperature	Substrate composition	% TS Content	Recirculation rate
1	2	78	50	37°C	60:40 Sludge : Rice husk	15	6X
2	4	49	28				
3	6	68	24				
4	8	35	18				

Table 6 gives details of operational conditions during batch start-up phase. It is mentioned in table that temperature and solid content are maintained in mesophilic range as 37⁰ C and 15%. Substrate of sludge and rice husk is used throughout the tenure with eventual increase of organic loading rate. Recirculation rate of 6 time of fresh feed is maintained throughout the operational phase. Reactor was operated at OLR of 2 kg VS/m³/day for 87 days and 35 days for OLR of 8 kg/Vs/m³/day. Operation time is kept double as compare to retention time to have reliable results. Equal amount of digestate is withdrawal from reactor as much as daily loading was done.

The total capacity of the reactor employed in batch start-up phase experiment was 40L, digester was loaded only once at the start of the experiment. For the continuous digestion, the digester was fed after every 24 hours with the substrate i.e. 0.2 kg of feed was fed for organic loading rates of 2 kg VS/m³/d with recirculation of with recirculation of 1.5 kg of digestate present inside of reactor.0.50 kg of feed was fed for organic loading rates of 4 kg VS/m³/d with recirculation of with recirculation of 3 kg of digestate present inside of reactor.0.6 kg of feed was fed for organic loading rates of 6 kg VS/m³/d with recirculation of with recirculation of 3.6 kg of digestate

present inside of reactor. 0.8 kg of feed was fed for organic loading rates of 8 kg VS/m³/d with recirculation of with recirculation of 5.1 kg of digestate present inside of reactor. Total solid content was maintained at 15% throughout the semi-continuous phase. It was achieved by addition of water in the feed. Recirculation rate was 6X of daily feed and equivalent amount of feed was discharged from outlet during semi-continuous operation. Details of OLR's are given in table 7.

Table 7 Operational Conditions

OLR (kg VS/m³/d)	Weight of Feed (kg)	Recirculation Weight (kg)	%TS of feed from Lab	Final TS %
2	0.25	1.5	49	15
4	0.501	3.0	47.28	15
6	0.67	4.0	47.89	15
8	0.85	5.1	49.3	15

Feeding of sludge and rice husk was enhanced eventually after stability of parameter after each run. Starting from low organic rate i.e. 2 kg VS/m³/d till 6kg VS/m³/d. 4th OLR was enhanced from 3rd directly i.e. 6 kg VS/m³/d to 8 kg VS/m³/d.

3.4 Analytical methods

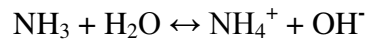
Below mentioned are operational and functional parameters of both dry anaerobic digesters, which were monitored throughout the digestion phase.

3.4.1 pH

pH inside the reactor was maintained between the ranges of 6.7 to 7.9 as the testing of pH of digestate in the laboratory on daily basis was done by biogas meter.

3.4.2 Ammonia-nitrogen

Ammonia-nitrogen is an essential nutrient that encourages growth of bacteria at lesser amounts. Anaerobic degradation of wastes with high protein content releases nitrogen in either in shape of dissolved free ammonia or ion of ammonium depending upon pH of system. Ammonia combines with water and carbon dioxide to make ammonium bicarbonate which acts as pH buffer. For AD processes, ammonia amounts in 50 and 200 mg/l in form of nitrogen are usually in ranges. Though, NH_3 is inhibitory at upper values and toxic if the concentration is much enough. NH_3 is a weak base and detaches in water in below mentioned form



There are numerous mechanisms proposed for NH_3 inhibition as enhancement of maintenance energy, variation in intracellular pH and inhibition of a precise enzyme reaction. NH_4^+ amounts in range 319 to 992 mg/l as nitrogen are successfully treated in absence of a toxic reaction with an adapted culture, although concentrations as low as 1500 mg/l as N can be toxic.

Ammonia inhibition can be more severe to the methanogens among the four types of anaerobic microorganisms, affecting their growth (Kayhanian, 1994) Ammonia is determined twice a week in the lab by following Kjeldahl distillation and titration method.

3.4.3 Alkalinity

Alkalinity is the buffering ability of water for neutralization of acids. Alkalinity is degree of bicarbonates, carbonates, hydroxides, and, occasionally, silicates, borates, and phosphates. It is stated in milligrams equal of CaCO_3 per liter. The methane forming (methanogens) in AD are affected by small pH changes, although the acid forming bacteria can operate reasonably in a wide range pH. Digestion constancy is subjected to the buffering ability of the reactor constituents. Its higher values indicate more capacity for resisting pH variations. Alkalinity value in this anaerobic reactor ranges in 4710 and 20660 mg/L. It is measured through titration method twice a week.

3.4.4 Volatile fatty acids

Volatile fatty acids buildup is the major cause of pH drops in anaerobic reactors with insufficient alkalinity. Volatile fatty acids concentrations above 2000 mg/l can be inhibitory to methanogens. VFA are weak acids that are mostly dissociated at neutral pH. As pH stays in the normal range for methanogenic growth (7.2-8.6), inhibition caused by volatile fatty acids is not significant since high concentration of volatile fatty acids is tolerated. When pH gets lower than this range, pH exerts considerable impacts which will be forced by any inhibition by non-ionized volatile fatty acids. Volatile fatty acids in this setup are ranged between 2404 to 7890 mg/l.

Volatile fatty acids is measured in the laboratory was measured by titration method twice a week.

3.4.5 Total solids determination

TS are the measure of (TDS) and (TSS) in water. It is usually is measured in mg/L. TS is measured in the laboratory by oven drying method twice a week.

3.4.6 Volatile solid

VS are such solids in water or other liquids which are lost on heating dry solids at 1020°F (550°C). It is a water quality measure attained from the loss on heating of TSS. Volatile solids were measured twice a week in lab by using muffle furnace.

3.4.7 Volume measurement of biogas

As the anaerobic reaction continues biogas is produced. That produced biogas was calculated through a wet tip biogas meter on daily basis. A pipe through the digester's biogas outlet was joined to wet tip biogas meter. This biogas meters measured the units if biogas generated and those units were then converted into volume of biogas by making proper gas expansion calculations according to the ambient temperature measured per day. Table 8 illustrates the expansion of gas at a given temperature.

Table 8 Biogas expansion according to ambient temperature

Ambient Temperature	1 biogas unit is equal to
10°C	13 ml
15°C	14 ml
20°C	15 ml
25°C	16 ml
30°C	17 ml
35°C	18 ml

With every 5°C enhance in ambient temperature there is 1ml enhance in biogas expansion. As temperature inside the reactor was maintained at 35°C, every unit of biogas generated was multiplied by 18 ml.

CHAPTER 4

Results and Discussion

This chapter is classified in two parts. In part 1st, anaerobic digestion of prepared feed is investigated during its batch phase. In second phase different organic loadings are evaluated in terms of their biogas production potential. The feed used in batch phase consisted of substrate and inoculum. Inoculum source consists of Digestate 13.5 kg obtained from a mesophilic dry anaerobic reactor and cow dung 6.5 kg. 60:40 mixture of sludge and rice husk is used. Total solid maintained at 15% TS by addition of water. This mixture was used in batch phase for acclimatization and stabilization of reactor.

After running batch phase 4 organic loadings of 2, 4, 6 and 8 kg VS/m³/d were analyzed with same sludge and rice husk ratio and %TS.

The results of the study are discussed below.

4.1 Start-up of mesophilic dry anaerobic digester in pilot-scale experiment

For start-up phase of pilot scale experiment, 50% of the reactor's working volume was fed by inoculum that included a combination of cow dung and digestate of a mesophilic anaerobic reactor. Rest of 50% of working volume was occupied with substrate consisting of rice husk and sludge in 60:40 with adjusted TS of 15%. The temperature of reactor was maintained (37°C) which is in mesophilic range. It was achieved by thermostatically temperature controlled setup. During initial 82 days which is start-up phase of reactor homogenization of the digester feed was carried out at rate of 15% of total feed/day and nothing was added. Details of parameters is as under

4.1.1 pH

As shown in figure 7, the pH was initially 6.72; the reason of this low pH is accumulation of volatile fatty acids during gathering of sludge for substrate perpetration of batch phase. As a result, slight amounts of NaOH were added to the reactor in period of first 22 days to keep pH close to neutral limits. It is visible as minor increments of pH in span of 11-15 days in Figure 6. After day 24 and ahead, pH had not declined another time and initiated progressing gradually, so sodium hydroxide was not used any longer.

pH of reactor stabilized around 7.7 during the span of 60-80 days.

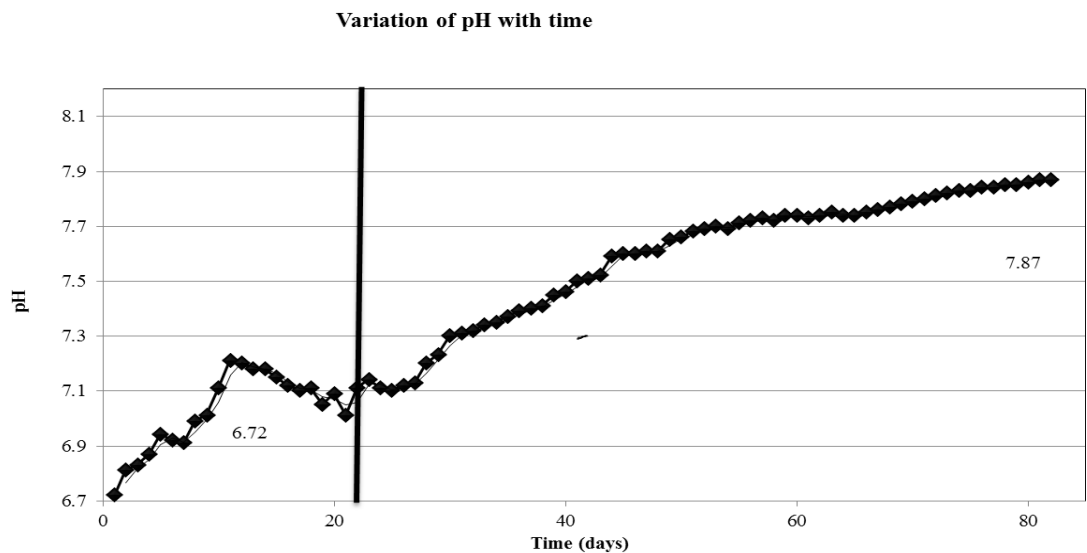


Figure 7 Variation of pH during start-up

4.1.2 VFA

As shown in figure 8 initially, the amount of volatile fatty acids enhanced as the reactor was loaded and reached to its highest of (11318 mg/L) on day 19. Volatile fatty acids of sludge is intrinsically low but it was accumulated during gathering sludge for batch phase. But, as the pH attained stable conditions, volatile fatty acids quantity started declining because of its consumption. The quantity of volatile fatty acids declined from 11318 to 9203 mg/L only in 20 days. The cause of this variation was that no feed was wasted or discharged during the span of start-up phase.

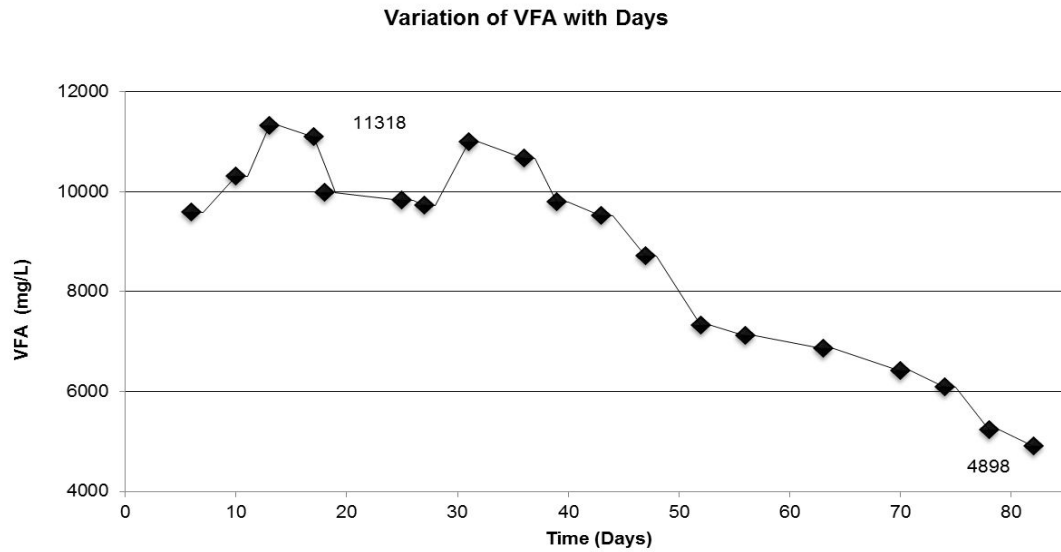


Figure 8 Variation of VFA during start-up

4.1.3 VFA/Alk

As shown in figure 9, the variation of volatile fatty acids to alkalinity ratio was same as volatile fatty acid quantity. Initial progression of volatile fatty acids/Alk ratio after reactor loading was observed till day 11 then there was a constant decline that shows, alkalinity initiated to progress and enhanced after loading. It could be so as a fraction of inoculum that was employed for this start-up phase was collected from the setup which was in similar circumstances (treating sludge and cow dung under mesophilic conditions). After day 30, volatile fatty acids/alk ratio declined similar as that of volatile fatty acids. This can be referred to decline in volatile fatty acids concentration.

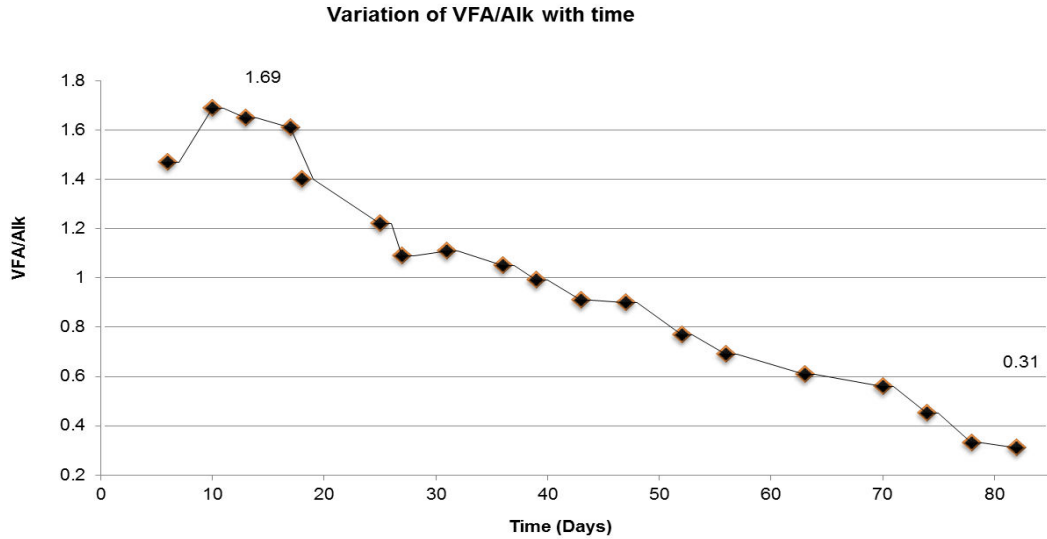


Figure 9 Variation of VFA/Alk in batch start-up

4.1.4 Biogas generation rate

Biogas generation rate was lesser in the start as shown in figure 10. The cause can be undesirable environment for methanogenic activity, i.e., pH lesser to 6.8 and volatile fatty acids more than range of 6000-8000 mg/L (Polprasert, 2007). Though, biogas generation rate initiated to progress gradually as the system advanced to constancy as pH and alkalinity enhanced and volatile fatty acid got consumed.

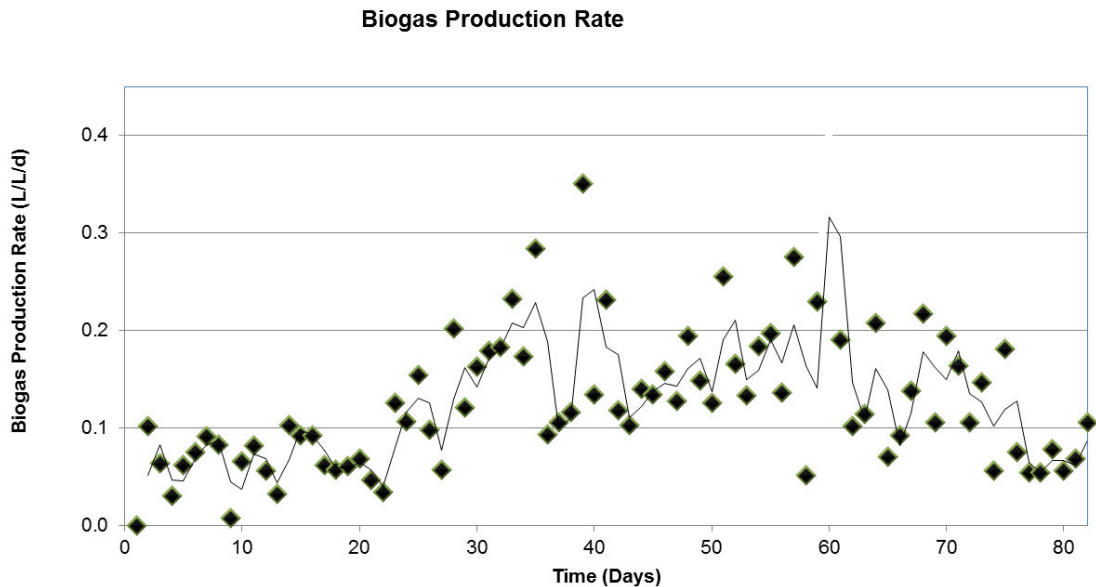


Figure 10 Variation of biogas production rate in start-up phase

By above facts, it can be established that volatile fatty acids and pH amounts in digester were not stabilized till day 30, therefore, methane content was less, content of carbon dioxide could be higher and GPR was not stable. Anyhow, after day 35, the digester environment was steady and, so, GPR is enhanced. Comparative to other studies, this start-up phase took moderately more time in reaching constant conditions. The cause might have been higher recirculation rate i.e. 15% as well as accumulation of anaerobic conditions may have taken time as feed preparation took around 15 days. Secondly a major portion of substrate in start-up

Phase is rice husk, which was added to control bio-degradability of sludge. At completion of start-up phase, gas production rate declined, that can be due to most of the built up volatile fatty acids was consumed by microbes as illustrated by rise in pH and decline in volatile fatty acids. This indicates the completion of batch startup

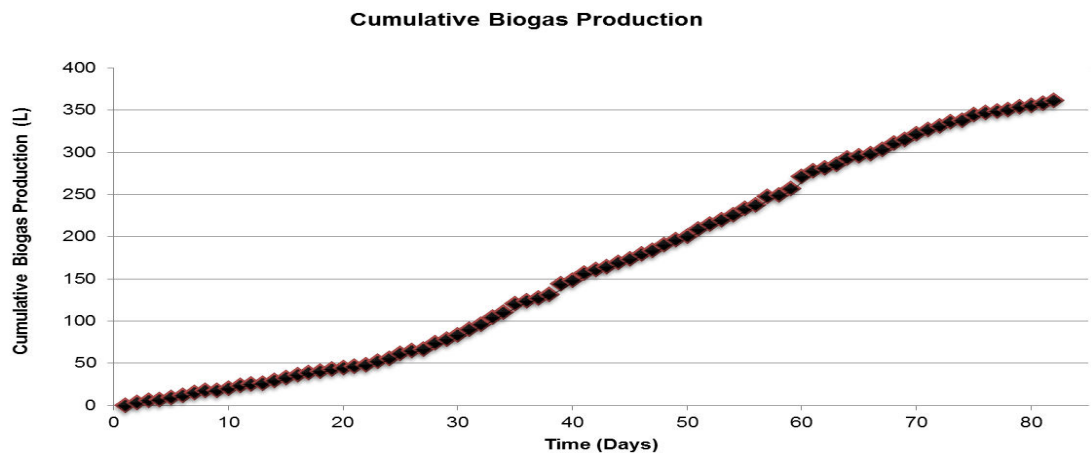


Figure 11 Cumulative biogas production during batch start-up

Phase where continuous digester loading should be initiated. Figure 11 is indicating cumulative biogas production which indicates the sharpness during the maturation phase i.e. from day 40-60.

4.1.5 Ammonia nitrogen

Figure 12 shows the variation of ammonia-nitrogen during batch start-up phase. Effect of inhibition is controlled by keeping C: N of 30 by addition of mixture of 60:40 of sludge and rice husk.

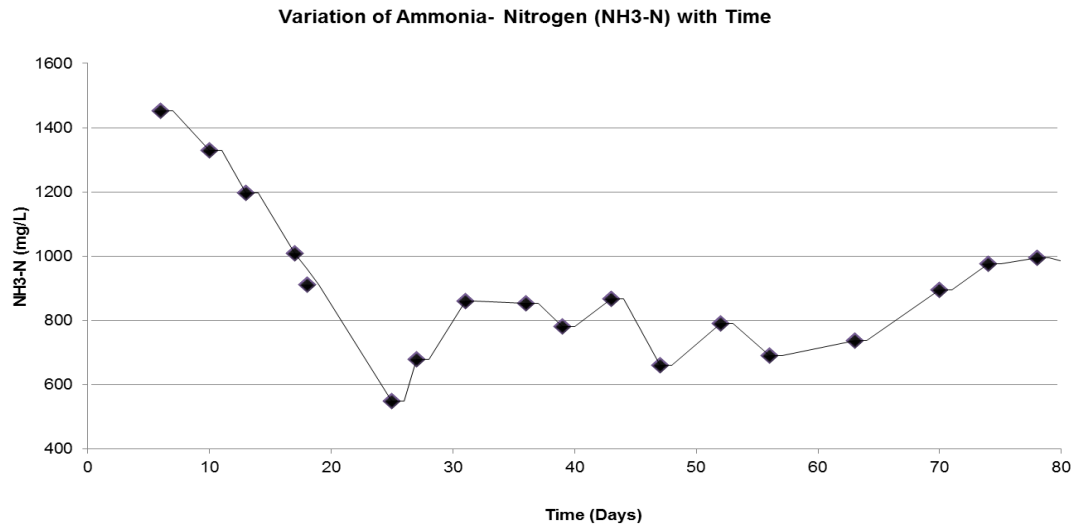


Figure 12 Variation in ammonia-nitrogen during batch start up

It was concluded from this research that batch start-up phase completed (at nearby day 82) when much amassed volatile fatty acids were consumed by microbes and its amount declined from 11318 mg/L at day 12 to 6000 mg/L on day 71 and more reduced to 4838.81 mg/L on day 82. With this reduction in volatile fatty acids, pH enhanced from 6.82 to 7.87 and the stability of reactor conditions touched its supreme by attaining the least volatile fatty acids to alkalinity ratio of 0.31. So the conclusion of batch start-up phase was declared by the least values of volatile fatty acids/Alk ratio and volatile fatty acids concentration. Similar results were obtained in literature (Slimane et al., 2014).

Furthermore, by assessment of start-up phases of related tests, it was established that low recirculation of digestate should be employed to attain stable conditions of reactor in a small of time.

4. 2 Effect of organic loading on stability parameters during semi-continuous phase rate

4.2.1 pH

pH is fundamental stricture to assess the strength during anaerobic digestion. When organic loading rate was 2 kg VS/m³ /d, the setup normalized its pH at near 7.65 in range of 7.5-7.8 as presented in Fig. 13 as OLR was enhanced from 2 to 4 kg VS/m³/d, pH dropped to 7.4 and normalized to an average of 7.63 (7.35-7.95). Consequently further progression in organic loading rate to 6 kg VS/m³ /d, a significant decline in pH had been witnessed and pH varied to 7.69.

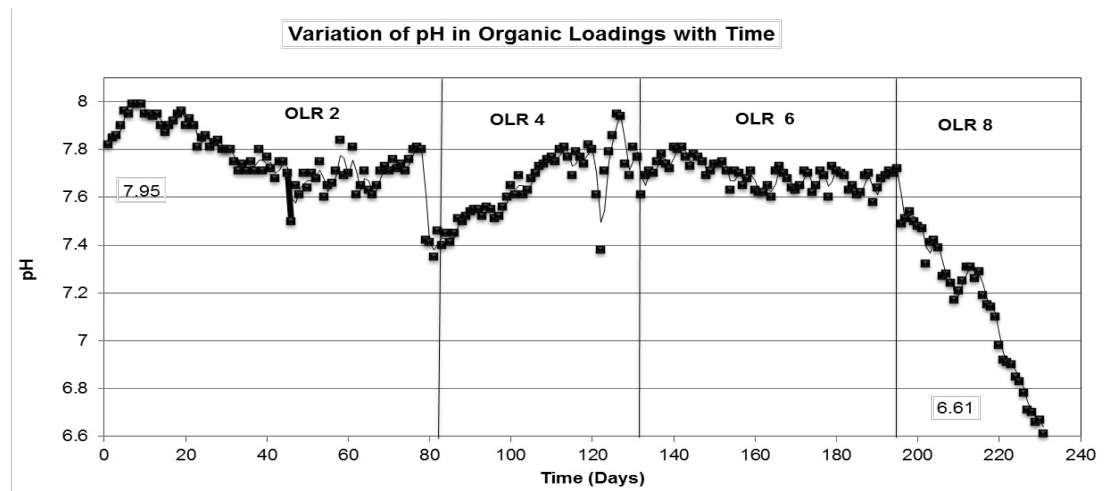


Figure 13 Variation of pH during semi-continuous phase

Retention time was enhanced for self-optimization of pH. The lessening of pH during initial span of both of the initial two OLR and much of the last run is related to disruption of the system as a consequence of enhancing OLR. The cause is that as OLR is enhanced the acidogenic bacteria too enhance their activity and generate high quantity of volatile fatty acids, as they have quick growth. But contrary, methanogens because of slow specific growth rate of theirs cannot consume all the already generated volatile fatty acids and require additional time to form the mandatory population extent. So temporary and initial reduction in pH is because of accumulation of volatile fatty acids as a consequence of this unevenness in the groups of microorganisms that is retrieved till methanogenic bacteria form their ample

population. The reduction of pH is more distinct when functioning with elevated OLR, i.e., 6-8 kg VS/m³/d. The cause is the disproportion among acidogenic and activity of methanogens is further prominent.

4.2.2. Volatile fatty acids

With reference of figure 14, the quantity of volatile fatty acids in digestate material of mesophilic dry anaerobic reactor was much constant on average values of 5190 mg/L (range: 4131-5609 mg/L) on functioning at OLR of 2 kg VS/m³/d. As organic loading rate was increased to 4 kg VS/m³/d, volatile fatty acids concentration started decreasing and approached a lowest of 2409 mg/L with an average of 3254 mg/L (2404-3666mg/L) in this turn. This shows the stability of system. At organic loading rate of 6 kg VS/m³/d, volatile fatty acids concentration enhanced to 3736 (range: 2669-4890 mg/L) and 5890 mg/l (range: 4478-7890 mg/L) at organic loading rate 8 kg VS/m³/d because of enhanced OLR.

This tendency displays the destabilization of the reactor because of enhancing organic loading rate.

This is significant to note that at beginning of every organic loading rate, volatile fatty acids started to amass, which that can be referred with unevenness of activity of microorganisms and initial temporary imbalance of reactor as a result of enhancement in organic loading rate as discussed above as of pH. Similarly, at the completion of each of first two organic loading rates, the quantity of volatile fatty acids declined, which is a sign of constancy of the system. Anyhow, this decline in volatile fatty acids concentration for organic loading rate of 6-8 kg VS/m³/d was not detected probably as the setup at this phase was functioned for period equivalent to only one cycle of solid retention time.

Further to that, the increase of OLR from 6-8 kg VS/m³/d was not gradual this sudden enhance is pronounced in volatile fatty acids values at OLR 8.

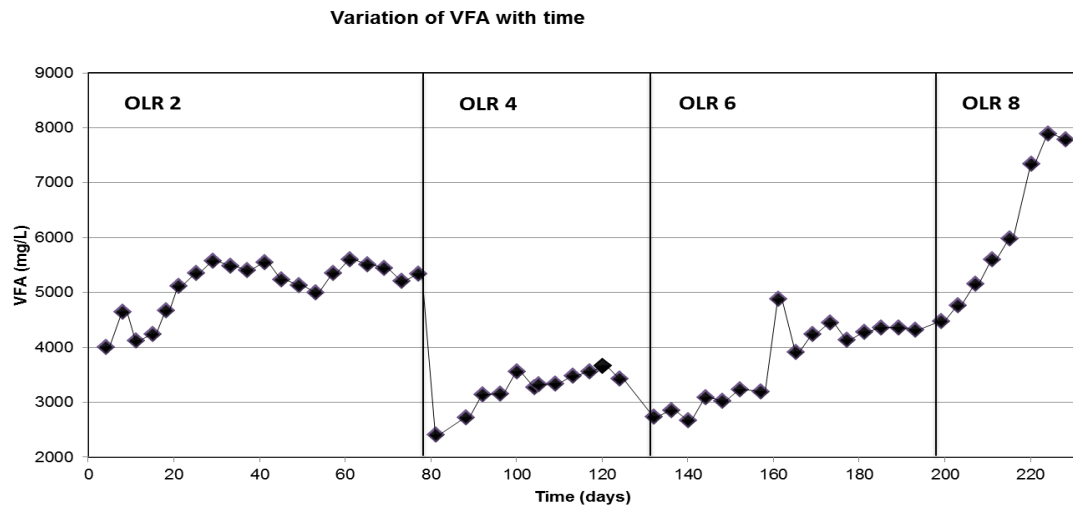


Figure 14 Variation of VFA during semi-continuous phase

Amount of volatile fatty acids and pH are opposite to each other. A low pH assists the generation of volatile fatty acids (acidogenic bacterial activity), that in turn subdues volatile fatty acids utilization (methanogenic activity). That can be described by our results too.

4.2.3. Volatile fatty acids to alkalinity ratio VFA/Alk)

Volatile fatty acids/alkalinity ratio is a good gauge of digester operation. With organic loading rate of 2 kg VS/m³/d, this parameter persisted among 0.35 (range: 0.27-0.44) for maximum duration (Figure 15). That is a fine range of volatile fatty acids/alkalinity ratio for an operational digester. But at organic loading rate 4 kg VS/m³/d, average value of volatile fatty acids/alk ratio enhanced to 0.42 (range: 0.35-0.53) that is too satisfactory for an operational reactor. Though, at organic loading rate of 6 kg VS/m³/d, volatile fatty acids/alkalinity ratio enhanced to very damaging range 0.68 (range: 0.60-0.80), because at volatile fatty acids/alkalinity ratio of 0.8, substantial pH reduction and digester failure occurs (Khannal, 2008). At OLR 8 kg VS/m³/d

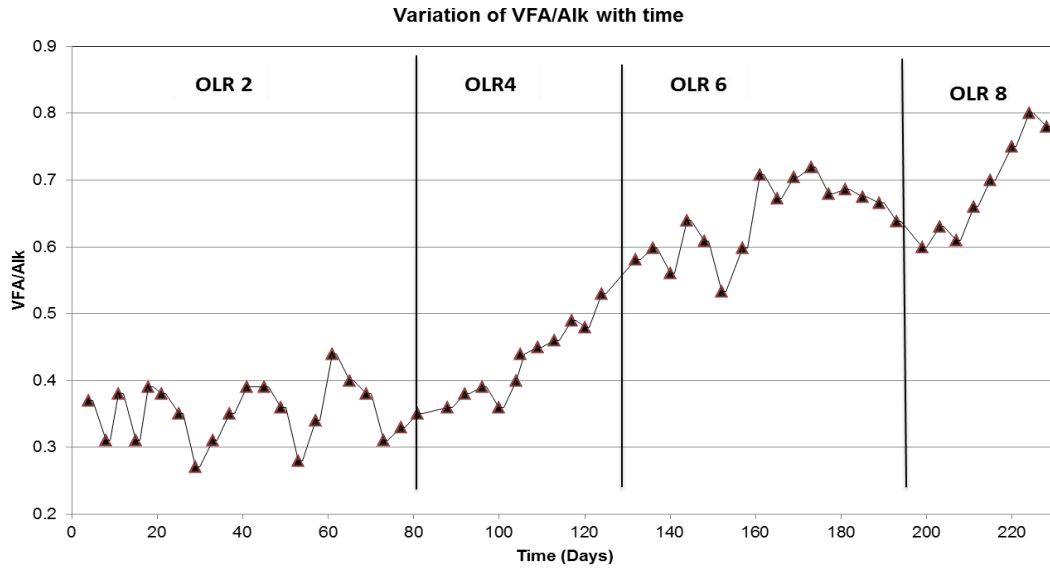


Figure 15 VFA/Alk variation during semi-continuous phase

Volatile fatty acids/alk reached to average value of 0.72 (range: 0.6-0.81) which led to Volatile Fatty Acids inhibition of reactor and feeding was stopped.

4.2.4 Ammonia-nitrogen

In figure 16 it is shown that similar to batch phase effect of ammonia inhibition has been controlled by a designed feed with adequate C: N ratio of 28. Sludge: Ratio was

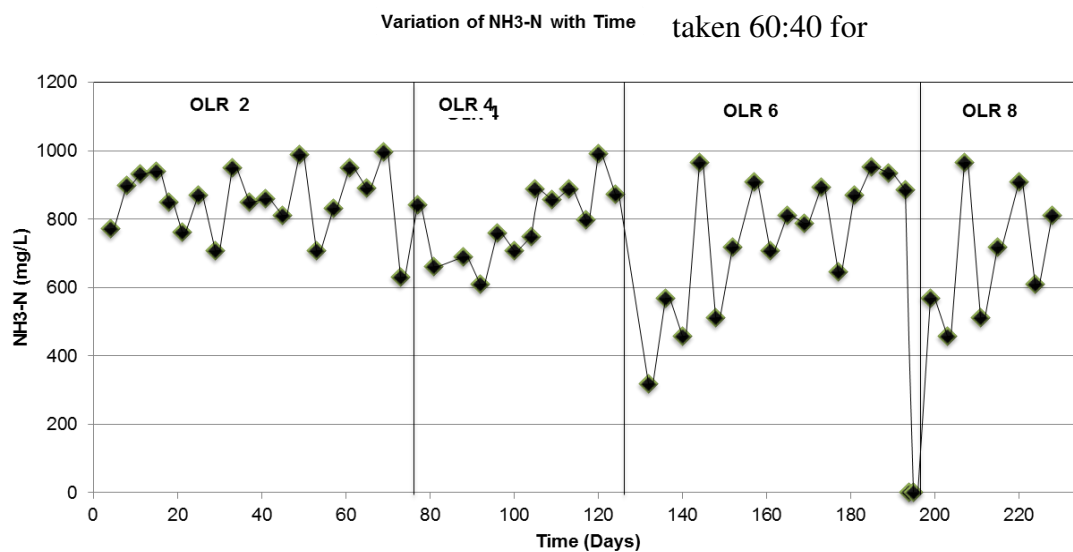


Figure 16 Variation of ammonia-nitrogen with time

All OLR's. This has neglected the effect. For OLR 2 kg VS/m³/ day ammonia-nitrogen averaged on 852 mg/L (range: 631-995 mg/L). For OLR 4 kg VS/m³/ day it averaged around 789 (range: 610-990 mg/L). For OLR 6 kg VS/m³/ day it averaged around 746 (Range: 319-965 mg/L) and for OLR 8 kg VS/m³/ day it is around 723 (Range: 456-965 mg/L)

4.3 Effects of OLR on performance parameters during semi-continuous phase

4.3.1. Gas generation rate

Gas Generation rate was enhanced in OLR 2 and 4 kg VS/m³/d with value of 0.24 and 0.43 L/L reactor vol. /d correspondingly comparing it to OLR 6, where gas generation rate was 0.86 L/L_{reactor} vol. /d. Figure 17 indicates biogas generation rate of mesophilic dry anaerobic reactor as L/L_{reactor} volume/d in several phases of semi continuous loading phase. At the end of organic loading rate 2 and 4 kg VS/m³/d, the gas generation rate tends to be stable. This is associated with stable pH and volatile fatty acids concentration of the setup at the stated period.

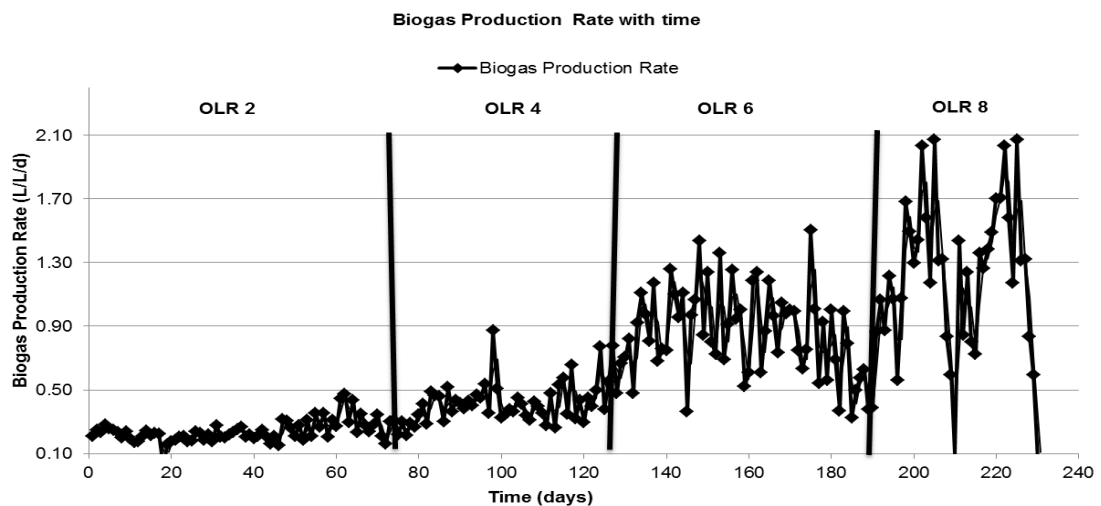


Figure 17 Variation of biogas production rate in semi-continuous phase

The enhancement in gas generation rate was almost linear with enhancement in organic loading rate in first two turns. But, in run 3 and 4 (i.e. organic loading rate 6

an 8 kg VS/m³/d), the gas generation rate did not enhanced as same as that of organic loading rate. That can be described by significant enhancement in volatile fatty acids/alk ratio (or decline in alkalinity) in that run. As stated before OLR 8 has been enhanced directly from OLR 6. This caused destabilization of reactor and inconsistent biogas production. As effect of overloading can be lessened by further adapting the reactor in those circumstances.

4.3.2. Specific biogas yield (SBY) and removal of volatile solids

The Volatile Solids removal was maximum in OLR 2 kg VS/m³/d. Therefore, the best results on kg VS basis were shown at OLR of 2 kg VS/m³/d are in terms of digestate quality, as shown in Table 9 the obtained VS removal of 76.42%. From figure 18 it is shown that maximum biogas generation per unit weight of volatile solids added is also called specific biogas yield, SBY was obtained at OLR of 6 kg VS/m³ /d 142 L /kg VS whereas it was 20% lower for OLR 8 kg VS/m³ /d. However, biogas production by all the runs of this study provided in appendix B, in accordance with the biogas yield values in literature

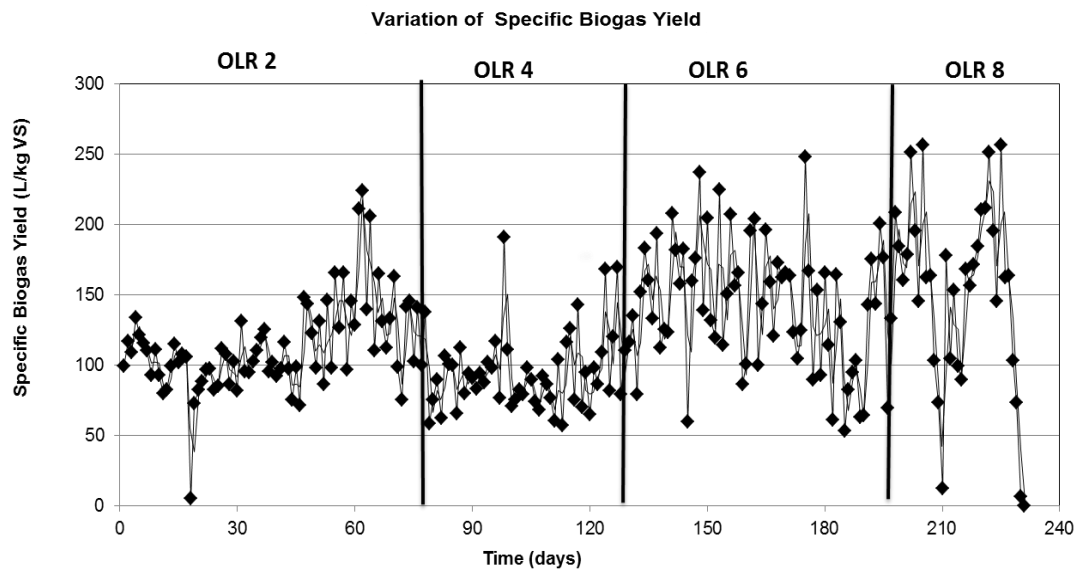


Figure 18 Variation of specific biogas yield in semi-continuous phase

Table 9 indicates %VS removal has decreased with increase of organic loading rates. The ability of reactor to convert accumulated volatile fatty acids has declined that is

indicated by decreased %VS removal in OLR 8 kg VS/m³/d and highest VS removal is indicated when OLR is lowest i.e. 2 kg VS/m³/d.

Table 9 Percentage of VS removal and specific biogas yield

OLR kg VS/m ³ /d	Volatile Solids Inlet kg VS	Volatile Solids Outlet kg VS	Volatile Solids Loss %	SBY L Biogas /kg VS
2	60.6	16.54	76.42	113
4	66.7	26.21	60.54	94
6	66.18	29.7	63.15	142
8	67.6	32.12	47.18	114

These results are similar to those obtained by (Montero et al., 2008). A comparison of OLR 4 and 6 indicates that performance in terms of specific biogas yield and %VS removal is better in case of OLR 6 kg VS/m³/d. Comparable outcomes have too been stated in last studies (Duan et al., 2012; Somashekar et al., 2014), in which VS elimination declined with enhancement in TS content of digestate

4.4. Comparative analysis

It is to understand here that volatile fatty acids/alk jumped at once during OLR 6-8. Because enhancing of OLR was done directly as compared to previous successions where there was gradual enhance. The tendency of volatile fatty acids/alk ratio

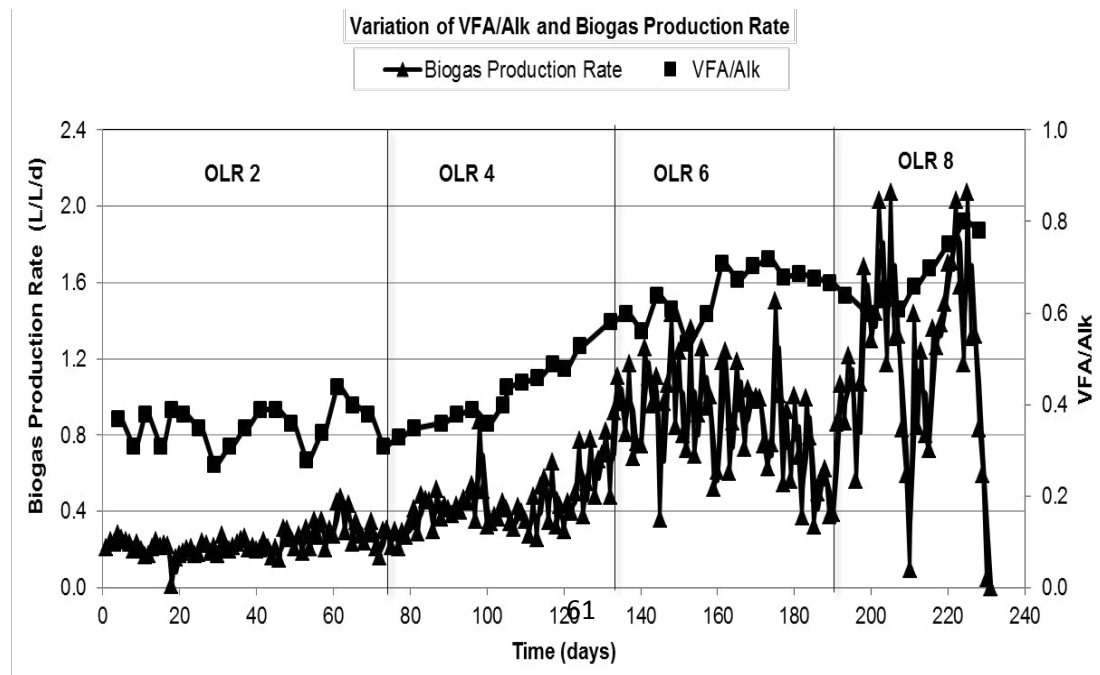


Figure 19 Comparative variation of biogas production rate and VFA/Alk

Nearly shadowed the trend of volatile fatty acids concentration (Figure 19), as volatile fatty acids concentration enhanced and volatile fatty acids/alk ratio followed it. Therefore, growth in volatile fatty acids concentration displays any hostile effect on this ratio and therefore performance of system.

In figure 19 variation of biogas production rate is shown in comparison with volatile fatty acids/Alk ratio. It indicates that during enhance in volatile fatty acids/Alk enhanced destabilization of reactor. Drop in SBY along-with %VS elimination at higher OLR's was too detected by (Zeshan et al., 2012)

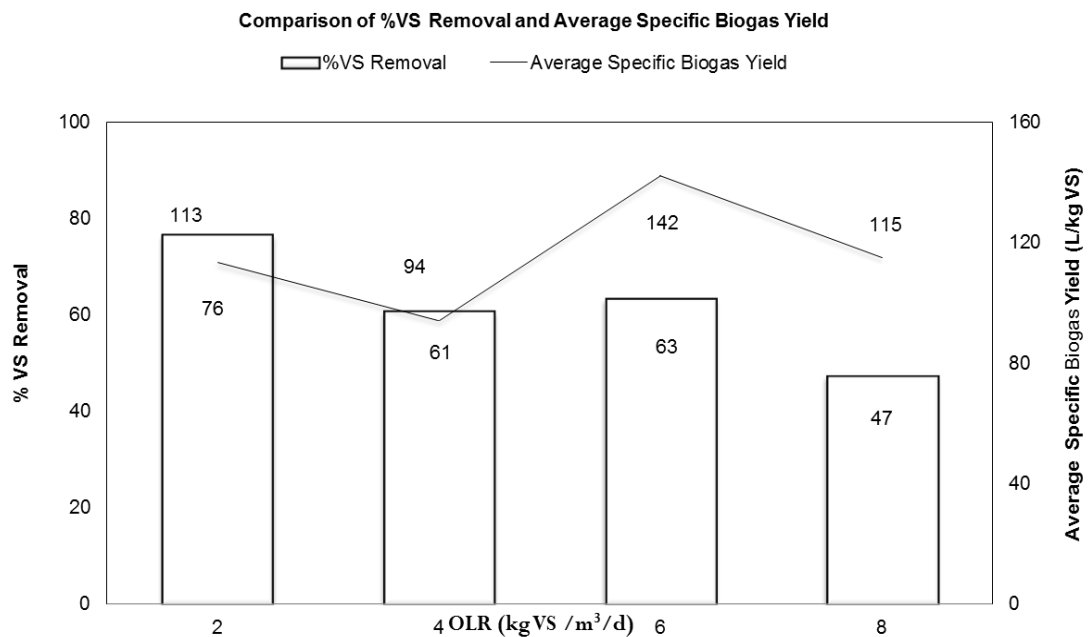


Figure 20 Comparative analysis of %VS removal and average specific biogas yield.

Figure 20 is comparative analysis of %VS removal along-with average specific biogas yield. Highest %VS removal is in OLR 2 but SBY is lower. In OLR 8, SBY is moderately better but %VS removal has declined sharply. Comparing OLR 4 and 6, %VS removal has minor dissimilarity but the difference in SBY is quite remarkable.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

This research examined the operation and construction of dry anaerobic digestion of sludge mesophilic phase obtained by membrane bio reactor along with rice husk at different organic loadings to evaluate maximum biogas production.

Single scale semi-continuous dry anaerobic pilot scale reactor was used for of this study. First batch phase, 1st, 2nd and 3rd Organic loading of 2, 4, 6. Final 8 kg VS/m³/day were studied. Effect of variation of organic loading rate was analyzed on operation of dry anaerobic co-digestion. Biogas production was used as quantitative measure.

The conclusions drawn from detailed study are mentioned in the following section.

5.1 Conclusions

Below mentioned are recommendations made for further studies concluded from the research conducted:

- Decreasing trend of stability of the reactor was observed between OLR of 8kg VS /m³/d as pH dropped, VFA and VFA/Alk increased drastically.
- On OLR 6 kg VS/m³/d reactor was more stable as compared to OLR 8 kg VS/m³/d
- % VS removal along with biogas production was higher and consistent at OLR 6 kg VS/m³/d than OLR 8 kg VS/m³/d and 4 kg VS/m³/d.
- 6 kg VS/m³/d is considered to be the most optimum OLR for sustainable dry anaerobic co-digestion of sludge and rice husk.

5.2 Recommendations

Below mentioned are recommendations made for further studies concluded from the research conducted:

- Effect of pre-treatment of said substrate can be considered for future studies for stability and enhancement of biogas production.
- Effect of recirculation and varying temperature ranges need to be analyzed for dry anaerobic co-digestion of subjected substrate.
- Step wise progression of OLR during semi-continuous phase is recommended for sustainable dry anaerobic co-digestion at higher organic loading rates.
- Digestate management is not considered in this research. Behavior of intended substrate as fertilizer after digestion needs to be studied.

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Appendix A Data of Batch Phase Experiment

Table A Operational Parameters of Anaerobic Digestion during Batch Phase

Days	pH	Biogas Reading	Volume of Bio Gas Liters	Biogas Production Rate (L/L/d)	Specific Biogas Yield L/kg VS	%TS	%VS(%TS)	Ammonia mg/L	Alkalinity mg/L	Volatile Fatty Acids mg/L	Volatile Fatty Acids/alk
1	6.72	0	0	0.00	0	15.00	70.1				
2	6.81	198	4	0.10	2						
3	6.83	321	2	0.06	1						
4	6.87	379	1	0.03	0						
5	6.94	498	2	0.06	1						
6	6.92	643	3	0.07	1	15.00	64.67	145	6521	9587	1.47
7	6.91	821	3	0.09	2						
8	6.99	981	3	0.08	1						
9	7.01	995	1	0.01	0						
10	7.11	1123	2	0.07	1	17.98	61.53	1328	6101	10312	1.69
11	7.21	1281	2	0.08	1						
12	7.20	1389	2	0.06	1						
13	7.18	1451	1	0.03	0	17.54	56.81	1196	6859	11318	1.65
14	7.18	1651	4	0.10	2						
15	7.15	1831	3	0.09	2						
16	7.12	2011	3	0.09	2						
17	7.10	2131	2	0.06	1	16.76	50.96	1008	6893	11098	1.61
18	7.11	2241	2	0.06	1			910	7131	9983	1.40
19	7.05	2359	2	0.06	1						
20	7.09	2491	2	0.07	1						
21	7.01	2581	2	0.05	1						
22	7.11	2647	1	0.03	0						
23	7.14	2891	4	0.13	2						
24	7.11	3099	4	0.11	2						
25	7.10	3398	5	0.15	3	11.10	48.64	54	8048	9819	1.22
26	7.12	3588	3	0.10	2						
27	7.13	3698	2	0.06	1	10.98	41.93	678	8918	9721	1.09
28	7.20	4091	7	0.20	4						
29	7.23	4326	4	0.12	2						
30	7.30	4642	5	0.16	3						
31	7.31	4991	6	0.18	3	14.94	41.21	86	9909	1100	1.11
32	7.32	5346	6	0.18	3						
33	7.34	5798	8	0.23	5						
34	7.35	6135	6	0.17	3						
35	7.37	6687	9	0.28	6						

36	7.39	6868	3	0.09	2	13.09	40.98	852	10163	10671	1.05
37	7.40	7073	3	0.11	2						
38	7.41	7298	4	0.12	2						
39	7.45	7981	12	0.35	7	10.64	40.71	780	9897	9798	0.99
40	7.46	8241	4	0.13	2						
41	7.50	8691	8	0.23	5						
42	7.51	8921	4	0.12	2						
43	7.52	9121	3	0.10	2	12.76	40.52	866	10451	9511	0.91
44	7.59	9393	4	0.14	3						
45	7.60	9654	4	0.13	2						
46	7.60	9961	5	0.16	3						
47	7.61	10209	4	0.13	2	11.27	38.09	659	9680	8712	0.90
48	7.61	10587	6	0.19	4						
49	7.65	10876	5	0.15	3						
50	7.66	11120	4	0.13	2						
51	7.68	12658	8	0.26	5						
52	7.69	12981	5	0.17	3	14.33	37.1	789	9506	7320	0.77
53	7.70	13240	4	0.13	2						
54	7.69	13598	6	0.18	4						
55	7.71	13981	6	0.20	4						
56	7.72	14245	4	0.14	2	10.05	36.11	689	10317	7119	0.69
57	7.73	14781	9	0.28	6						
58	7.72	14881	1	0.05	1						
59	7.74	15328	8	0.23	5						
60	7.74	16110	14	0.40	8						
61	7.73	16481	6	0.19	4						
62	7.74	16679	3	0.10	2						
63	7.75	16901	4	0.11	2	13.38	35.09	736	11239	6856	0.61
64	7.74	17304	7	0.21	4						
65	7.74	17441	2	0.07	1						
66	7.75	17621	3	0.09	2						
67	7.76	17889	4	0.14	3						
68	7.77	18312	7	0.22	4						
69	7.78	18517	3	0.11	2						
70	7.79	18894	6	0.19	4	10.70	34.85	895	11449	6411	0.56
71	7.80	19212	5	0.16	3						
72	7.81	19418	3	0.11	2						
73	7.82	19703	5	0.15	3						
74	7.83	19812	1	0.06	1	12.27	33.24	975	13535	6091	0.45
75	7.83	20164	6	0.18	3						
76	7.84	20309	2	0.07	1						
77	7.84	20414	1	0.05	1						
78	7.85	20519	1	0.05	1	9.63	32.87	994	15851	5231	0.33
79	7.85	20671	2	0.08	1						

80	7.86	20779	1	0.06	1						
81	7.87	20912	2	0.07	1						
82	7.87	21118	3	0.11	2	6.49	70.1	964	15802	4898	0.31

Appendix B. Data of Semi Continuous Phase Experiment

Table B Operational Parameters of Anaerobic Digestion during Semi-Continuous Loading Phase

Days	pH	Biogas Meter Reading	Volume of Bio Gas (L)	Specific Biogas Yield (L/kg VS)	Biogas Production Rate (L/L/d)	TS%	% VS (% TS)	Ammonia mg/L	Alkalinity mg/L	Volatile Fatty Acids mg/L	Volatile Fatty Acids/Alk
1	7.82	2409	7	99	0.21						
2	7.85	2891	8	116	0.25						
3	7.86	3341	8	109	0.23						
4	7.9	3891	9	133	0.28	7.6	69.30	771	10847	4013	0.37
5	7.96	4391	9	121	0.26						
6	7.95	4867	8	115	0.24						
7	7.99	5320	8	109	0.23						
8	7.99	5703	6	92	0.20	7.1	42.18	898	15004	4651	0.31
9	7.99	6161	8	111	0.24						
10	7.95	6543	6	92	0.20						
11	7.95	6871	5	79	0.17	8.9	67.96	931	10873	4131	0.38
12	7.94	7209	6	81	0.17						
13	7.95	7619	7	99	0.21						
14	7.9	8091	8	114	0.24						
15	7.87	8510	7	101	0.22	9.1	54.10	940	13695	4245	0.31
16	7.9	8954	7	107	0.23						
17	7.92	9390	7	105	0.22						
18	7.95	9411	1	5	0.01	8.6	56.93	850	11997	4678	0.39
19	7.96	9710	5	72	0.15						
20	7.9	340	6	82	0.17						
21	7.93	702	6	87	0.19	11.6	39.05	761	13481	5123	0.38

22	7.9	1101	7	96	0.21						
23	7.81	1503	7	97	0.21						
24	7.85	1843	6	82	0.17						
25	7.86	2193	6	84	0.18	10.6	65.60	870	15304	5356	0.35
26	7.81	2654	8	111	0.24						
27	7.83	3097	7	107	0.23						
28	7.84	3453	6	86	0.18						
29	7.8	3876	7	102	0.22	11.31	45.22	707	20660	5578	0.27
30	7.8	4212	6	81	0.17						
31	7.8	4751	9	130	0.28						
32	7.75	5145	7	95	0.20						
33	7.71	5534	7	94	0.20	9.61	50.51	950	17702	5487	0.31
34	7.74	5955	7	102	0.22						
35	7.71	6409	8	110	0.23						
36	7.75	6901	8	119	0.25						
37	7.71	7416	9	124	0.26	8.61	68.46	850	15463	5412	0.35
38	7.8	7810	7	95	0.20						
39	7.71	8230	7	101	0.22						
40	7.77	8609	6	91	0.19						
41	7.72	9010	7	97	0.21	10.71	54.90	860	14246	5556	0.39
42	7.68	9489	8	116	0.25						
43	7.75	9891	7	97	0.21						
44	7.75	10201	5	75	0.16						

45	7.7	10608	7	98	0.21	9.1	55.05	810	13445	5243	0.39
46	7.5	10901	5	71	0.15						
47	7.65	11510	10	147	0.31						
48	7.61	12101	10	143	0.30						
49	7.7	12605	9	122	0.26	9.16	66.32	989	14252	5134	0.36
50	7.64	13008	7	97	0.21						
51	7.7	13549	9	131	0.28						
52	7.68	13904	6	86	0.18						
53	7.75	14505	10	145	0.31	10.17	48.27	707	17852	4998	0.28
54	7.6	14908	7	97	0.21						
55	7.65	15590	12	165	0.35						
56	7.66	16110	9	126	0.27						
57	7.71	16792	12	165	0.35	7.89	56.60	830	15750	5355	0.34
58	7.84	17191	7	96	0.21						
59	7.69	17790	10	145	0.31						
60	7.7	18320	9	128	0.27						
61	7.81	19189	15	210	0.45	8.93	55.59	950	12748	5609	0.44
62	7.61	20113	16	224	0.48						
63	7.65	20688	10	139	0.30						
64	7.71	21536	15	205	0.44						
65	7.63	21990	8	110	0.23	8.15	58.08	891	13778	5511	0.40
66	7.61	22670	12	164	0.35						
67	7.65	23209	9	130	0.28						

68	7.71	23671	8.	112	0.24						
69	7.73	24219	9	132	0.28	8.2	43.07	995	14329	5445	0.38
70	7.71	24891	12	162	0.35						
71	7.76	25298	7	98	0.21						
72	7.72	25608	5	75	0.16						
73	7.74	26190	10	141	0.30	9.7	53.13	631	16819	5214	0.31
74	7.71	26789	10	145	0.31						
75	7.76	27210	7	102	0.22						
76	7.8	27789	10	140	0.30						
77	7.81	28201	7	99	0.21	8.7	45.54	843	16194	5344	0.33
78	7.8	28769	10	137	0.29						
79	7.42	51220	9	58	0.27						
80	7.41	51891	12	75	0.35						
81	7.35	52689	14	89	0.41	8.9	44.8	661	6871	2404	0.35
82	7.46	53245	10	62	0.29						
83	7.4	54193	17	106	0.49						
84	7.45	55091	16	100	0.46						
85	7.41	55981	16	99	0.46						
86	7.45	56567	10	65	0.30						
87	7.51	57571	18.	112	0.52						
88	7.5	58281	12	79	0.37	8.2	36.87	690	7552	2718	0.36
89	7.52	59123	15	94	0.43						
90	7.54	59931	14	90	0.42						
91	7.55	60671	13	82	0.38						
92	7.55	61510	15	93	0.43	8.1	36.09	610	8273	3144	0.38
93	7.52	62290	14	87	0.40						
94	7.56	63198	16	101	0.47						
95	7.55	64071	15	97	0.45						
96	7.51	65116	18	116	0.54	7.1	39.98	760	8097	3158	0.39
97	7.52	65801	12	76	0.35						
98	7.56	67502	30	190	0.87						
99	7.6	68492	17	110	0.51						
100	7.65	69120	11	70	0.32	8.34	27.78	707	9900	3564	0.36
101	7.61	69789	12	74	0.34						

102	7.69	70523	13	82	0.38						
103	7.61	71231	12	79	0.36						
104	7.63	72103	15	97	0.45	8.76	29.45	750	8186	3274	0.40
105	7.68	72901	14	89	0.41	10.09	38.08	887	7548	3321	0.44
106	7.7	73560	11	73	0.34						
107	7.73	74167	10	67	0.31						
108	7.74	74990	14	92	0.42						
109	7.76	75761	13	86	0.40	11.34	54.37	856	7409	3334	0.45
110	7.77	76445	12	76	0.35						
111	7.75	76982	9	60	0.28						
112	7.8	77910	16	103	0.48						
113	7.81	78416	9	56	0.26	14.8	55.65	889	7562	3478	0.46
114	7.77	79451	18	115	0.53						
115	7.69	80572	20	125	0.58						
116	7.79	81245	12	75	0.35						
117	7.77	82521	22	142	0.66	7.1	34.34	798	7258	3556	0.49
118	7.74	83145	11	69	0.32						
119	7.82	83989	15	94	0.43						
120	7.8	84567	10	64	0.30	6.98	42.21	990	7637	3666	0.48
121	7.61	85439	15	97	0.45						
122	7.38	86210	13	86	0.40						
123	7.71	87180	17	108	0.50						
124	7.79	88679	26	167	0.77	7.5	36.21	873	6484	3436	0.53
125	7.86	89409	13	81	0.38						
126	7.95	90481	19	119	0.55						
127	7.94	91991	27	169	0.78						
128	7.74	933	16	79	0.48						
129	7.69	2232	23	110	0.67						
130	7.81	3598	24	115	0.70						
131	7.77	5191	28	135	0.82						
132	7.61	8905	16	79	0.48	10.16	44.8	319	4710	2739	0.58
133	7.69	10698	32	151	0.92						
134	7.71	12854	38	182	1.11						
135	7.7	14745	34	160	0.97						
136	7.75	16312	28	132	0.81	11.17	46.98	568	4764	2851	0.60
137	7.78	18591	41	193	1.17						
138	7.74	19914	23	112	0.68						
139	7.72	21389	26	125	0.76						
140	7.81	22841	26	123	0.75	10.32	38.91	456	4756	2669	0.56
141	7.8	25291	44	207	1.26						
142	7.81	27431	38	181	1.10						

143	7.77	29290	33	157	0.96						
144	7.73	31443	38	182	1.11	11.35	31.97	965	4844	3097	0.64
145	7.78	32147	12	59	0.36						
146	7.77	34031	33	159	0.97						
147	7.75	36106	37	175	1.07						
148	7.69	38901	50	236	1.44	11.16	36.19	511	4980	3030	0.61
149	7.71	40541	29	139	0.84						
150	7.74	42949	43	204	1.24						
151	7.74	44504	27	131	0.80						
152	7.75	45908	25	119	0.72	9.97	41.04	717	6060	3230	0.53
153	7.71	48554	47	224	1.36						
154	7.63	49899	24	114	0.69						
155	7.71	51670	31	150	0.91						
156	7.7	54110	43	206	1.25		38.96				
157	7.65	55950	33	155	0.95	10.98		909	5330	3190	0.60
158	7.68	57903	35	165	1.00						
159	7.71	58919	18	86	0.52						
160	7.63	60101	21	100	0.61						
161	7.62	62404	41	195	1.18	11.91	44.89	709	6903	4890	0.71
162	7.62	64810	43	203	1.24						
163	7.65	65990	21	100	0.61						
164	7.6	67680	30	142	0.87						
165	7.71	69990	41	195	1.19	10.17	51.43	810	5817	3913	0.67
166	7.73	71867	33	159	0.97						
167	7.7	73290	25	120	0.73						
168	7.68	75322	36	172	1.05						
169	7.64	77231	34	161	0.98	8.4	51.23	788	6023	4243	0.70
170	7.63	79180	35	165	1.00						
171	7.65	81111	34	163	0.99						
172	7.71	82563	26	123	0.75						
173	7.7	83791	22	104	0.63	5.9	50.42	893	6192	4452	0.72
174	7.62	85256	26	124	0.75						
175	7.65	88181	52	247	1.50						
176	7.71	90144	35	166	1.01						
177	7.69	91198	18	89	0.54	12.98	52.98	645	6091	4141	0.68
178	7.6	93001	3	152	0.93						
179	7.73	94091	19	92	0.56						
180	7.71	96042	35	16	1.00						
181	7.7	97385	24	113	0.69	10.23	54.92	870	6243	4282	0.69
182	7.69	98104	12	60	0.37						
183	7.63	100040	34	164	1.00						
184	7.65	101578	27	130	0.79						

185	7.61	102207	11	53	0.32	7.09	52.9	953	6457	4359	0.68
186	7.62	103178	17	82	0.50						
187	7.69	104291	20	94	0.57						
188	7.7	105507	2	103	0.63						
189	7.58	106244	13	62	0.38	6.16	50.12	936	6553	4364	0.67
190	7.64	106999	13	64	0.39						
191	7.68	108678	30	142	0.86						
192	7.69	110747	37	175	1.06						
193	7.71	112441	30	143	0.87	8.98	47.54	887	6769	4323	0.64
194	7.7	114809	42	200	1.22						
195	7.72	116890	37	176	1.07						
196	7.49	1090	19	69	0.56						
197	7.51	3178	37	138	1.07	10.11	49.7				
198	7.54	6451	58	207	1.68						
199	7.5	9354	52	184	1.49		66.18	568	7464	4478	0.60
200	7.48	11876	45	160	1.30		66.18				
201	7.47	14859	50	178	1.44		66.18				
202	7.32	16994	71	251	2.03		66.18				
203	7.41	19890	55	195	1.58		46.98	456	7571	4769	0.63
204	7.42	234889	41	145	1.17	12.22	46.98				
205	7.39	27908	72	256	2.07						
206	7.27	31093	45	161	1.31						
207	7.28	35658	46	163	1.32	11.17	48.91	965	8460	5161	0.61
208	7.24	38980	29	102	0.83						
209	7.17	41540	20	73	0.59						
210	7.21	36106	3	12	0.10						
211	7.25	38901	50	177	1.44	10.32	41.97	511	8482	5598	0.66
212	7.31	40541	29	104	0.84						
213	7.31	42949	43	153	1.24						
214	7.26	44504	27	98	0.80						
215	7.29	45908	25	89	0.72	11.35	36.19	717	855	5990	0.70
216	7.19	48554	47	168	1.36						
217	7.15	2459	44	156	1.26						

218	7.14	5151	48	171	1.38						
219	7.1	8046	52	183	1.49	11.16	41.04				
220	6.98	11356	59	210	1.70			909	9793	7345	0.75
221	6.92	14679	59	211	1.71						
222	6.91	18632	71	251	2.03						
223	6.9	21707	55	195	1.58	9.97	48.96				
224	6.85	23989	41	145	1.17			609	9862	7898	0.80
225	6.83	28018	72	256	2.07						
226	6.78	30567	45	161	1.31						
227	6.71	33141	46	163	1.32						
228	6.7	34760	29	102	0.83	10.98	54.89	810	9986	7789	0.78
229	6.66	35916	20	73	0.59						
230	6.67	36012	1	6	0.05						
231	6.61	36012	0	0.00	0.00						

Annexure C Experimental Set-up Pictures



Figure 22 Lead Oxide coating on reactor outer body



Figure 21 Reactor Inner Cylinder



Figure 24 Reactor after construction



Figure 23 Assembling of water bath