Production of Biogas using pre-treated rice straw in a Plug flow Reactor

Thesis submitted in partial fulfilment of the requirements for award of the degree of Master of Bioprocess Engineering

Submitted by

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Personally I found the topic intriguing and it was a great learning experience to prepare the thesis on this.

Abhijit Barman

CERTIFICATION

This is to Certify that ABHIJIT BARMAN, final year Master of Bioprocess Engineering(MBPE) examination student of Department of Biprocess Engineering,Jadavpur University (Exam Roll no: M4BPE19007 Registration No: 140626 of 2017-2018) has completed the project work titled,"**Production of Biogas using pre-treated rice straw in a Plug flow Reactor"** under the guidance of **Dr. Chanchal Mondal** and **Smt.Sujata Sardar** during his post-graduation curriculum.This work has not been reported earlier anywhere and can be approved for submission in partial fulfilment of the course work.

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Abstract

Biogas is a modern energy source and its very suitable for our environment.The Biogas is very cost effective and can be produced easily.In the Laboratory the production of biogas is very effective and ecofriendly for our mankind.The Production of biogas by anaerobic digestion of the organic wastes like Rice Straw,Food and Vegetable waste etc is a mature expertise that gives more benifit to the Poultry Producers.Biogas is a source of non conventional energy is produced by fermentation of sludges. The modern biogas plants is the sources of the energy and are beneficial for our environment.Now a days biogas Production is usually applying in waste water treatment,mainly sewage sludge.Biogas is produced from the microbial decomposition of organic materials under anaerobic conditions.Cattle manure is also the best sample for the biogas production.From the cattle manure biogas can be prepared in a domestic way. It is the best source of electricity under low cost.

Contents

Particulars:

Introduction

Agricultural biogas production offers several environmental benefits. Electricity and heat are produced from a renewable energy source. Standardised guide lines on the buildings and the operations of agricultural biogas plants guarantee a cost effective building and save operation.Co- digestion of agricultural organic wastes is regulated,as well this helps to enhance the implementation of biogas technology on farms, anaerobic digestion of farmyard manure, the aim of agricultural biogas production in our country about 20% of farmyard and 40% of waste. Therefore it is important to get technical solutions for the digestion of slurry and farmyard manure. The development and put into practice biogas plants that offer the possibility of digesting slurry, farmyard manure and agricultural organic waste. This project describes the biogas technology and gives the better result on the performance of biogas plants that digest farmyard manure. The change of farmyard manure composition after anaerobic digestion and the amount of green house and gases that is emitted if the farmyard manure is not digested but stacked anaerobically. The anaerobic Digestion process is the most cost effective process for production ,it helps to our environment to make pollution free.It is also a most eco-friendly technology for our environment.The biogas Plants is now using the modern biogas process techniques to produce biogas for higher yield.

Literature Review

Biogas production and concentration of methane at various HRT(Hydrulic Retention Time), using 1, 2 and 4% TS (wt/vol) of a mixture of pulp and peel in the plug-flow reactor. Methane concentration from G3 was much higher than those from R2 and R1 at all combinations of % TS and HRT(Hydrulic Retention Time). The higher methane concentration recorded from R3 and R2 was due to the separation phase in the plug-flow reactor, allowing the reactor to behave as a two-phase system for acid phase (R1) and methane phase (R2 and R3), *(Bardiya et al., 1996).*

With a feed solid content of 1% (wt/vol), the decrease of HRT from 30 d to 7 d (thus increasing OLR from 0.11 to 0.46 kg COD/ m^3 d) resulted in a higher biogas production rate (from 0.01 to 0.06 v/v-d). As summarized in 1% TS (wt/vol) with HRT of 7 d resulted in biogas yield, 0.19 m^3/kg COD removed; methane yield, 0.07 m^3/kg COD removed; biogas production rate, 0.06 v/v-d; and COD removed, 74.9%. The increase of feed solid concentrations of substrate from 1 to 24% (wt/vol) at HRT 10 d showed increases in biogas yield, methane yield, and biogas production rate. However, there was a significant decrease in conversion of the substrate into biogas when HRT was reduced to 5 d for 1 and 2% TS (wt/ vol), and 7 d for 4% TS (wt/ vol),*Sunggrinhorm (2002).*

Anaerobic digestion enhancement:

As discussed, significant effort has been dedi- cated in recent years to find ways of improving the performance of digesters treating dierent wastes, es- pecially solid wastes, because of the obvious link be- tween successful pre-treatments and improved yields. These treatments can be biological, mechanical or physico-chemical. The economic aspects of digestion enhancement are very important to industry, a point not usually covered in the studies reported.

Among biological methods of improvement, *(Capela et al. 1999)* report the in¯uence of a pre-composting treatment on the start-up and performance of dry an- aerobic digestion of pulp mill sludge. The eect was clearly visible through methane yields and consequently solids reduction which were greater than in the digestion of untreated sludge. In the same line of pre-treatment, *(Hasegawa and Katsura.1999)* reported a 50% im- provement in yields when sewage sludge was solubilised under *slightly thermophilic aerobic conditions prior to anaerobic digestion.* They suggest that thermophilic aerobic bacteria secrete external enzymes which dissolve sludge more actively than commercial proteinase. A similar study has also been carried out in a pilot plant in which there is an aerobic step before a leaching opera- tion takes the lixiviates to an anaerobic reactor *(Wel- linger et al., 1999)*.

The classic addition of complexes of enzymes has been carried out recently by *(Rademacher et al.1999)* to improve the efficiency of anaerobic sewage sludge di- gestion,*(Scheidat et al.1999)* who added to thickened municipal primary sludge a mixture of pep- tidases, carbohydrolases and lipases (from 0% to 10% on TS) which is significantly improved hydrolysis at 39°C and 51°C. However they did not study the technical and economic feasibility of this addition, which are key points in the application of these methods.

Fig 1: Chemical Structure of Lignocellulosic Biomass(Rice Straw)[50]

Biogas Production Potential of Rice Straw:
Biogas is the form of energy produced when microorganisms decompose organic matter in the anaerobic digestion process. Biogas is primarily composed of methane and carbon dioxide *(Lane, 1984, 1985; Vandevivere et al., 2003)*.
with trace amounts of hydrogen sulphide, ammonia and water vapor. Methane produced from Organic Waste.*(Lane, 1984, 1985; Vandevivere et al., 2003)*
biomass is a clean, renewable energy source that currently represents approximately 12% of the global energy consumption.

and is the primary source of energy for over half of the

world's population. Fewer air pollutants and less carbon dioxide per unit of energy are released when compared with non-renewable fossil fuels.Europe is the leading producer of biogas with Germany clearly at the forefront. And maize Using food crops for energy production is controversial because the demand for food is expected to increase in the future and food prices are likely to rise as a result,*(Tanticharoen et al. 1984)*

Food security is a top global priority and using lignocellulosic materials such as rice straw for energy production does not interfere with that priority. The use of agricultural waste products is more desirable because of high availability and reduced greenhouse gases released into the atmosphere when the waste products are utilized rather than left in the field to decompose. When compared with six other lignocellulosic biomasses (wheat straw, oat straw, barley straw, sorghum straw, corn stover and sugar cane bagasse), rice straw was selected as the most favorable feedstock for energy production primarily because of the quantity available,*(Rani and Nand,2004)*.

Though the organic matter is not completely converted by the anaerobic digestion of rice straw, the remaining residues can be used as topsoil maintenance or sustainable growth for biomass .When considering factors such as purchase price, potential fuel yields, and environmental concerns, cellulosic biomass can significantly contribute to energy sustainability and security.

The methane potential, however, of untreated rice straw is on the lower end when compared to other agricultural biomasses and agro-industrial by-products. various food crops and agricultural by-products.*(Liu and Ghosh, 1997)*

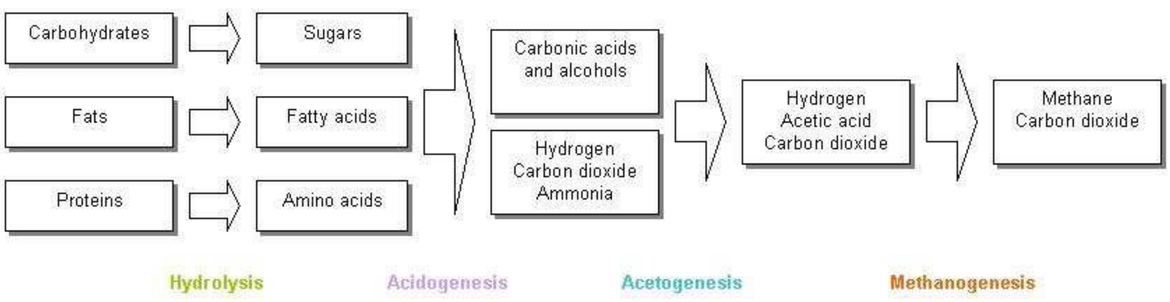


Fig 2:Different Stages of Anaerobic Digestion [40]

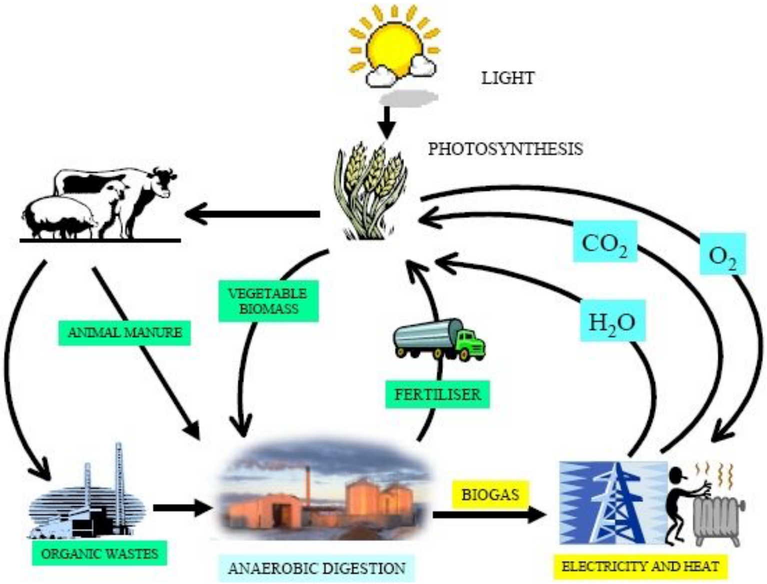


Fig 3: The Utility of the Biogas Production[50]

Rice straw is a lignocellulosic biomass that contains a relatively high lignin content (i.e. 10 to 15% dry weight), which makes it very difficult to degrade because the ligno- carbohydrate complexes form strong bonds and the plant cell wall is resistant to microbial attack. Lignin is a highly complex polymer that holds together the polysaccharide fibres and contributes to the structural rigidity of the straw. Thestructure of rice straw. So, a pretreatment step is often used to increase the degradability of the rice straw and accelerate the digestion process. Several approaches for pretreatment of rice straw have been investigated including physical (i.e. size reduction), biological (i.e. fungi), and chemical (i.e. acid and alkali additions). Mechanical size reduction of the rice straw ruptures the cell walls and makes the organic matter more readily available for the microorganisms to decompose. Milling, or cutting, the biomass exposes more surface area and reduces the polymerization, which leads to an increased hydrolysis of the lignocellulosic biomass . The milling of lignocellulosic materials has resulted in increased methane yields (5 to 25%) and reduced digestion times (23 to 59%) . With all other variables held constant, the methane yield was slightly higher for rice straw that had been cut in 25-mm lengths (198 L/kg VS) versus rice straw that was digested whole (190 L/kg VS). In a study with wheat straw, the increase observed in the methane yield from 30-mm lengths (145 L/kg VS) compared to 1-mm lengths (161 L/kg VS) was significant after 60 days of digestion . However, the milling process requires high energy inputs and is not economically feasible. *(EurObserv'er. Biogas Barometer. Le Journal des Energies Renouvelables 2010;200:104).*

Advantages of Producing Biogas:

Biogas is Eco-Friendly:

Biogas is a form of the renewable energy, as well as a clean, source of energy. Gas generated through biodigestion is non-polluting; it actually reduces greenhouse emissions (i.e. reduces the greenhouse effect). No combustion takes place in the process, meaning there is zero emission of greenhouse gasses to the atmosphere; therefore, using gas from waste as a form of energy is actually a great way to combat global warming.*(German Agency for Technical Cooperation GmbH ,GTZ), 1999.*

Biogas Generation Reduces Soil and Water Pollution:

Overflowing landfills don't only spread foul smells- they also allow toxic liquids to drain into underground water sources. Consequently, yet another advantage of biogas is that biogas generation may improve water quality. Moreover, anaerobic digestion deactivates pathogens and parasites; thus, it's also quite effective in reducing the incidence of waterborne diseases. Similarly, waste collection, and management, significantly improve in areas with biogas plants. This, in turn, leads to improvements in the environment, sanitation, and hygiene.*(Scientific Research and Essays, vol. 4, no. 9, pp. 861–866, 2009).*

Biogas Generation Produces Organic Fertilizer:

The by-product of the biogas generation process is enriched organic (digestate), which is a perfect supplement or substitute for, chemical fertilizers. The fertilizer discharge from the digester can accelerate plant growth and resilience to disease.cause food poisoning, among other things be relatively low.*(Scientific Research and Essays, vol. 4, no. 9, pp. 861–866, 2009).*

It's A Simple and Low-Cost Technology That Encourages A Circular Economy:

The technology used to produce biogas is quite cheap. It is easy to set up and needs little investment when on a small scale. Small biodigesters can be used right at home, utilizing kitchen waste and animal manure. A household system pays for itself after a while, and the materials used for generation are absolutely free. The gas manifested can be used directly for cooking and generation of electricity. *(A. Cesaro and V. Belgiorno)"Pretreatment methods to improve anaerobic biodegradability of organic municipal solid waste fractions," Chemical Engineering Journal, vol. 240, pp. 24–37, 2014).*

Healthy Cooking Alternative For Developing Areas:

Biogas generators save women and children from the daunting task of firewood collection. As a result, more time is left over for cooking and clean. More importantly, cooking on a gas stove, instead of over an open fire, prevents the family from being exposed to smoke in the kitchen. This helps prevent deadly respiratory diseases. Sadly, 4.3 million people a year die prematurely from illness attributable to the household air pollution caused by the inefficient use of solid fuels for cooking. *(Scientific Research and Essays, vol. 4, no. 9, pp. 861–866, 2009)*.

Disadvantages of Producing Biogas:

Few Technological Advancements:

An unfortunate disadvantage of biogas today is that the systems used in the production of biogas are not efficient. There are no new technologies yet to simplify the process and make it abundant and low cost. This means large scale production to supply for a large population is still not possible. Although the biogas plants available today are able to meet some energy needs, many governments are not willing to invest in the sector.*(Scientific Research and Essays, vol. 4, no. 9, pp. 861–866, 2009)*

Effect of Temperature on Biogas Production:

Like other renewable energy sources (e.g. solar, wind) biogas generation is also affected by the weather. The optimal temperature bacteria need to digest waste is around 37°C. In cold climates, digesters require heat energy to maintain a constant biogas production supply.*(German Agency for Technical Cooperation GmbH ,GTZ), 1999.*

Less Suitable For Dense Metropolitan Areas:

Another biogas disadvantage is that industrial biogas plants only makes sense where raw materials are in plentiful supply (food waste, manure). For this reason, biogas generation is much more suitable for rural and suburban areas.

The aim and Objectives are mentioned below for the project:

- Optimization of Process Parameters.
- Enhancement of biogas yield by AD of the pretreated Sample.
- Kinetic study of AD Process.

Scope of the Present Work:

Biogas plant uses bacteria to degrade wet organic matter like animal dung, human sewage or vegetable and food waste which produces biogas, which is a mixture of methane and carbon dioxide, and also a semi-solid residue. The biogas plant is used for biogas production and management of the cow dung safely. In the present energy situation of Nepal, where there is a large energy deficit, the use of biogas plants to produce energy can bring a new turning point in the energy sector. The construction and operation of family sized biogas is successful in Nepal. It is seemed to give emphasis on large sized biogas plants as there are several cattle farms and consequently huge potential for big biogas plants.It helps in our poultry Industry as well to make more benificial.More importantly this process of biogas plantation is most easier to produce the biogas for our environment as a better result and efficiency.

Anaerobic Digestion Process & Process kinetics

Anaerobic digestion is a natural biological process when bacteria break down organic substances in environments with no oxygen. A controlled enclosed version of the anaerobic breakdown of organic waste is a effective and eco-friendly process which exhibits methane as one of end products. Several research groups have shown that the AD process can be classified into four main stages: hydrolysis, acidogenesis and methanogenesis and acetogenesis as shown,Anaerobic fermentation significantly reduces the total mass of waste, generates solid or liquid fertilizer and yields energy.

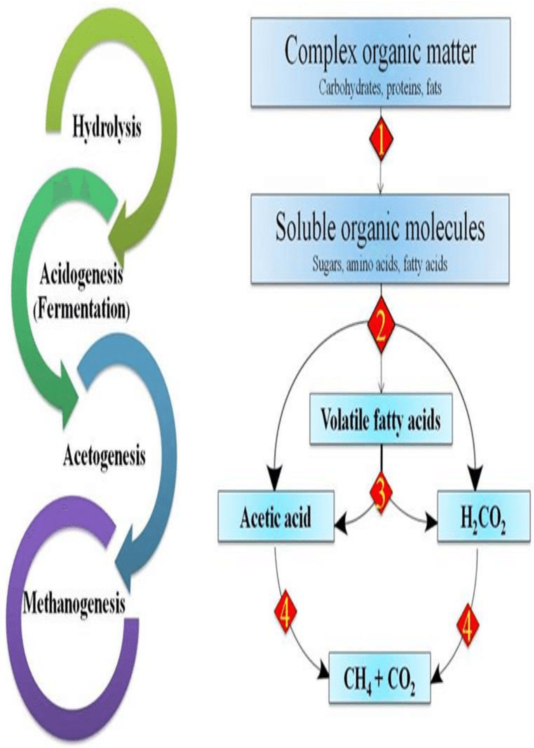


Fig 4: Steps of Anerobic Digestion

Hydrolysis:

A chemical process where particulates are solubilized and large polymers converted into simpler monomers.

Acedogenesis:

A biological conversion where simple monomers are converted into volatile fatty acid.

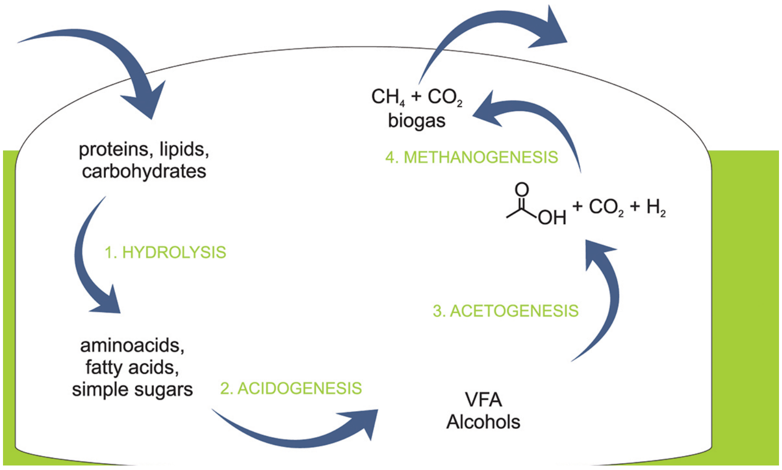


Fig 5: The Process of Anaerobic Digestion

Acetogenesis:

A biological conversion where volatile fatty acids are converted into acetic acid, carbon dioxide, and hydrogen.

Methanogenesis:

A biological conversion where acetate ions are converted into methane and carbon dioxide, while hydrogen is consumed.

Process Kinetics

Kinetic study of biogas production has been conducted for description and evaluation of methanogenesis by fitting the experimental data of biogas production to various kinetic equations.

It has been assumed that biogas pro- duction rate increases linearly with increase in time and after reaching a peak value it decreases linearly to a low significant value. The linear equation for biogas production rate can be expressed by the equation below:

1. $y = a + bT$

where y is biogas production rate (mL/g-VS/d)

T is hydraulic retention time in days and a and b are constants obtained from the intercept and slope of the graph plotted y versus T. Slope b is positive for the ascending limb and negative for the defending limb.

Consider,

2. $y = a + b^{cT}$

where y is biogas production rate (mL g^{-1} VS d^{-1}), T is hydraulic retention time in days

a (mL g^{-1} VS d^{-1}),b (mL$g^{-1}d^{-1}$),and c (day^{-1}) are constants,and c is positive for the ascending limb and negative for descending limb.

Consider,

$y = ae^{-0.5[(T-T_0)/b]^2}$,

where y is biogas production rate (mL g^{-1} VS d^{-1}), T is hydraulic retention time in days, T_0 is time at which the max- imum biogas production occurred, and a (mL g^{-1} VS d^{-1}) and b (day) are constants.

4. y= $a/1+be-kT$

where y is cumulative biogas production (mL g^{-1} VS), k is kinetic constant (day^{-1}), T is hydraulic retention time (days), and a and b are constants.

Consider

5.$y = ae-be^{-cT}$,

where y is cumulative biogas production (mL g^{-1} VS), T is hydraulic retention time (days), and a and b are positive numbers. a is biogas production potential (mL g^{-1}), b is min- imum time required to produce biogas (day), and c sets the growth rate (y-scaling), which are constants.

Consider

Process Parameters Affecting Methane Production

Temperature regime:

Thermophilic Anaerobic Digestion (55–70 1C) has a rate-advantage over mesophilic digestion as a result of its faster reaction rates and higher-load bearing capacity and, consequently, exhibits higher productivity compared with mesophilic AD. However, acidification may occur during thermophilic AD, inhibiting biogas production. Other disadvantages like decreased stability, low-quality effluent, more toxicity and susceptibility to environmental conditions, larger investments, poor methanogenis and higher net energy input have also been identified. In addition, this process is more sensitive to environmental changes than the mesophilic process. Although mesophilic systems exhibit better process stability and higher richness in bacteria, they afford low methane yields and suffer from poor biodegradability and disadvantages leading to nutrient imbalance.

pH:

The operational pH affects the digestive progress and products directly. The ideal pH range for AD has been done to be 6.8–7.5.VFA(Volatile Fatty Acid) composition based on carbon basis affected by pH.After reviewing of AD techniques for biogas production and relevant research progress is necessary and imperative for further biogas Production.

The aim and objective of this paper is to provide a comprehensive overview of AD research achievements in biogas production and to clarify the future outcome on of biogas production. Detailed information about factors affecting efficiency, accelerators, reactors and AD processes is listed based on the existing literature. This paper seeks to identify pathways toward optimizing of AD technology from a process perspective. Accordingly, benefits including cost savings and increased economic competiveness for biogas industrialized

The growth rate of microorganisms is significantly affected by pH changing. The relative abundance of microbial species has been observed to increase from 6 at pH 4.0 to 14 at pH 7.0 .At pH 6.0, the dominant bacterial population is Clostridium butyricum, whereas at pH 8, the Propionibacterium species appears to prevail during anaerobic acidogenesis with a chemostat culture . To reduce ammonia toxicity due to an increased concentration of free ammonia , controlling the pH level to attain optimum micro- organism growth represents one possible methodology. In a previous study, high extents of TSS and VSS degradation were obtained at pH levels of 7 and 8: 75% degradation of TSS and 85% degradation of VSS, whereas VFA showed no significant differences .

C/N ratio:

The C/N ratio reflects the nutrient levels of a digestion sub- strate, and thus, digestion systems are sensitive to C/N ratio. A high C/N ratio induces a low protein solubilization rate and leads to low TAN and FA concentrations within a system. Thus ammonia inhibition may be avoided by optimizing the C/N ratio in the AD process. However, an excessively high C/N ratio provides insufficient nitrogen to maintain cell biomass and leads to fast nitrogen degradation by microbials, resulting in lower biogas production and vice versa. Substrates with an excessively low C/N ratio increase the risk of ammonia inhibition, which is toxic to methanogens and causes insufficient utilization of carbon sources. The optimal C/N ratio for anaerobic digestion has been shown to be between 20 and 30 or between 20 and 35, with a ratio of 25 being the most commonly used.Insufficient amounts of carbon or nitrogen can limit AD performance in the anaerobic mono- digestion of livestock manure or crop straw.

OLR(Organic Loading Rate):

OLR represents the amount of volatile solids fed into a digester per day under continuous feeding. With increasing OLR, the biogas yield increases to an extent, but the equilibrium and productivity of the digestion process can also be greatly disturbed. Adding a large volume of new material daily may result in changes in the digester's environment and temporarily inhibits bacterial activity during the very early stages of fermentation. This bacterial inhibition occurs due to an extremely high OLR (Organic Loading Rate) leading to higher hydrolysis/ acidogenesis bacterial activity than methanogenesis bacterial activity and thus increases VFA production, which eventually leads to an irreversible acidification.

Retention time:

The retention time is the time required to complete the degradation of organic matter. It is associated with the microbial growth rate and it depends on the process temperature, OLR(Organic Loading Rate) and substrate composition.HRT 1⁄4 V Qwhere V is the biological reactor volume and Q the influent flow rate in time.An average retention time of 15–30 days is required to treat waste under mesophilic conditions. Obtaining an effective HRT(Hydrulic Retention Time) depends on the substrate composition and OLR, typically, a couple of weeks are necessary. Decreasing the HRT usually leads to VFA accumulation, whereas, a longer than optimal HRT results in insufficient utilization of digester components.

Composition of Biogas:

Table : 1

Typical Composition of Biogas		
COMPOUND	MOLECULAR FORMULA	PERCENTAGE
Methane	CH_4	50–75
Carbon Dioxide	CO_2	25–50
Nitrogen	N_2	0–10
Hydrogen	H_2	0–1
Hydrogen Sulphide	H_2S	0–3
Oxygen	O_2	0–0

Experimental Details

Preparation of Sample

Untreated Rice Straw is collected from a Cattle Field of Golfgreen and dried the sample and Milled for cutting in our lab and used for the Pretreatment.'Rice straw', as a lignocellulosic biomass, is comprised of three components: lignin, cellulose, and hemicelluloses.

Flow Chart of the Work

Step 1. Sample Collection

Step 2.Granding & Sorting

Step 3. Drying

Step 4: Cutting

Step 5: Maleration

Step 6: Pretreatmen(Chemical Pretreatment-Alkaline Pretreatment using KOH)

Step 7: Anaerobic Digestion in PFR

Step 8: Biogas-Methane.

Proximate Analysis of Biomass:

Proximate Analysis is a way to determine the distribution of products when the samples are heated under specified conditions.

Table:2

Table :I Proximate Analysis Sample:Rice Straw				
%MC	**%VM**	**%ASH**	**%FC**	**%TS**
14.37	67	13.33	5.29	85.62

% MC= 14.37 ± 0.3

%VM=67 ± 0

%ASH=13.33 ± 0.57

%FC=5.29 ± 0.75

%TS= 85.62± 4.35

MC: Moisture Content

VM:Volatile Matter

TS:Total Solid

FC:Fixed Carbon

Ultimate Properties of the sample (CHN Analysis):

Table:3

Sample	Carbon(%)	Hydrogen(%)	Nitrogen(%)
Pretreated	39.41	4.79	0
Untreated	36.99	4.76	0

Ultimate Analysis is done to analyse the % of Carbon,Hydrogen,and Nitrogen for Pretreated and untreated Sample.

FTIR (Fourier Transformed infrared Spectroscopy Analysis): For Functional group detection FTIR is Required.*The Perkin Elmer Spectrum-2 machine* is used for the FTIR Analysis.The Image of the FTIR Spectroscopy for Pretreated and Untreated Rice Straw is shown in the next Results and Discussions.

XRD(X-Ray Diffraction): The X-Ray diffraction is required for the Crystallinity Index of the sample.CI is a quantitive indicator of crystallinity of the sample.*The Rigaku,Ultima-III Diffractometer* machine is used for the XRD Analysis.The Separate graphs for Pretreated and Untreated Rice Straw is shown in the Results and Discussion.

SEM(Scanning Electron Microscope): The SEM is required to understand the morphology of the Sample for Pretreated and Untreated Rice Straw.The Figures are shown in the Results and Discussion Section.

Pretreatment

A pretreatment is something which is applied to a feed in order to make a process or stage more effective. A typical pretreatment prior to metal stripping

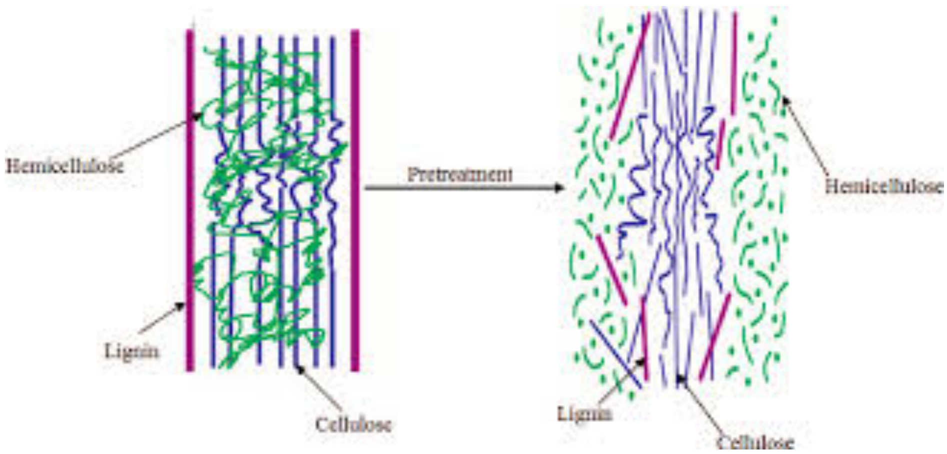


Fig 6:Pretreatment of the Lignocellulosic Biomass[46]

usually includes a soak in a *hot alkaline* cleaner followed by thorough rinsing.

Apparatus Required: 1000ml Beaker,Conical flask,PH paper,Distilled Water,Magnet,Stirrer.KOH,Wt.Balance.

Pretreatmet Method:

During the first step of pretreatment, 50 gm of untreated Rice Straw taken after cutting and washing and 1000 mL of distilled water at given concentration of KOH at room temperature.

- ➢ Sample was stirred in a magnetic stirrer for 3.5-4:00hrs.
- ➢ Wsh the sample with distilled Water until the PH reaches to 7.
- ➢ Rice Straw was dried in a Drying Machine.
  ➢ Used for Digestion
- **Biomass Yield: 30.5*100/50=61%**

Estimation Of Lignin: TAPPI Method-Acid Soluble

Rice Straw is a lignocellulosic biomass which contains about 12-14% lignin, a natural resinous material which acts as a binder for the cellulose and other materials involved in the structural skeleton of rice straw and other land plants. Rice Straw is now a days being chemically modified for newer and diversified environmental and domestic uses. For the purpose, lignin content of rice straw is either modified or degraded partially which becomes more sulphonated and goes into solution during hydrolysis with sulphuric acid.

Apparatus Required:

Flask,Filtering Crucible,Water Bath,Condenser,Hot Air Oven.

Procedure:

Step 1: Sulphuric Acid is taken(98.8%) and then 72% diluted in 300ml of Water. Step 2:Dry the Sample.

Step 3: 15ml sulphuric acid is taken in 100ml Beaker then cool it in Ice bath(During dispersion).

Step 4: Beakers is to be converted at (20 +/- 1) degree. Step 5: Keep the solution for 2hrs and stirr it frequently. Step 6: Add 3-400ml of water is to be transferred.
Step 7: Boil for 4 hr the entire solution.

Step 8. After boiling keep this solution overnight.

Step:Pour in each crucible for each sample for pretreated and untreated and after filtering wash out the crucibles and then dry the crucibles in the hot air oven then take the weight.
Lignin is estimated by the following equations:

Lignin,%= A*100/W
•Where A=Wt. of lignin,gm. *[**Process triplicated**]

Fig 7: Process of Lignin the Lignin estimation

Table:4

Untreated Rice Straw	Treated Rice Straw
12%	9%

PH is Measured at 7-Nutral

Optimization: The value is optimised.The action of making this is best or most effective use of a resource.

Calorific Value of Biomass

The Calorific Value is determined in a bomb calorimeter at constant volume precisely defined condition. These conditions must be adhered to since any alteration will cause a change in the determined calorific value.A sample of rice straw is burnt in oxygen in a bomb calorimeter of known heat capacity.The heat released is obtained from the corrected temperature rise of water in the calorimeter vessel.Deductions are made for :

- The constant heat gain due to heat release by the cotton thread and the firing wire.

- The difference between the heats of formation of sulphuric acid and sulphur di-oxide.

- The heat of formation of nitric acid.

In practice,the corrections are made as follows when the experiment is over,
a.Cooling correction.
b.Thermometer correction.
c.Correction for source of constant heat gainsay cotton threaded firing wire.
d.Correction for acids formed.

Cooling correction=V1(Ta-To)+V2(Tn-Ta) Where,

To=Time at Temperature t0 in minutes ,t0 is the temp. In degree cent at which firing is done.

Tn=Time at temperature tn in min,tn is the temp.in degree cent after which the rate fall of temp is constant.

Ta=Time at temp,[t0+0.60(tn-t0)mins.

V1=The rate of fall in temp per min in the preliminary period(When temp.rise V1 is negative).

V2=The rate of fall in temp per min in the after period. 6.6

Apparatus Required : Bomb Calorimeter,stop watch, chemical balance,wt box and pipette.

Procedure:

a.Prepare a SAMPLE PELLET weighing approx 1.0gm in the pelletising machine.

b.Weigh one metre of cotton thread accurately and take from it 20cm.Length thread for the expt.

c.Tie the thread properly to the coal pellet and weigh it.This weight less the weight of the thread will give you the weight of the sample taken.

d.Fix a pt wire of known wt(0.045 gm) to the poles of the bomb.Fasten the ends of the thread along with the coal pellet to the pt wire ana allow the pellet to rest on the crucible.

e.Add 10ml of distilled water to the bomb by means of a pipette.

f.Fill up the cal.Container with 2680ml of distilled water and place it on the tripod.

g.Place the bomb into the water of the cal container on the top of the tripod.

h.Immerse the stirrer in the water of the container,connect the bomb with the fire wires of the igniting current and place the cover on the top.

i.Introduce the thermometer into the apparatus ,put the stirrer into operation and fit up the thermometer lens.

j.When the temp in the cal meter is steady ,read off the data regularly after every min.

k.If the temp increases regularly and the difference remains unchanged for at least 3 mins consecutively,then at the beginning of the 4th min ignite the fuel by passing current for about 4-5sec.

l.After the ignition the temp increase very rapidly so that in the 1st and 2nd min the data are no longer quite correct. Note down the temp at an interval of one min until it reaches a maximum.

m.When the combustion is complete and the decrease of the temp per min is uniform, stop the experiment.

n.Now stop the stirrer, take out the thermometer and remove the error.

o.Disconnect the wires of the ignition current, take out the bomb from the cal container.

p.Dry the bomb,bomb, take out the crucible,weigh it properly and find out the ash content of the fuel.

q.Wash out properly the inside of the bomb and collect the liquid in a beaker.Keep it properly.   **Table:5**

Time (Min)	Temperature (°C)	Remarks
0	0,00	
1	0,06	
2	0,08	
3	0,09	Firing Point
4	0,11	
5	0,16	
6	0,20	
7	0,23	
8	0,24	
9	0,26	
10	0,27	
11	0,29	
12	0,30	
13	0,30	Constant temperature
14	0,30	Constant temperature
15	0,30	Constant temperature

So,t0=0.16°C & To= 5 mins & Tn=15mins & tn=0.30°C

Calculations:

Here V1=(0.09-0)/5=0.018 and V2=0 and ta=0.09+0.60(0.30-0.09)=0.216 mins.
Now Coolinng Correction applying Dickinson formula: V1(Ta-To)+V2(Tn-Ta)
So,the cooling Correction is:
0.018(6-5)+0=0.018

Wt.of cotton =0.00084gms
Wt of sample+paper=0.75gms
wt of pellet+Paper+cotton=1.70gms
wt.of pellet taken=0.01245gms
Now,The observed temperature rise = 0.11-0.09=0.02°C
Heat of combustion of to wire=4.6cal
Heat of combustion of the used cotton thread=4140*0.00838=34.6932 cal

Correction factor: 4.6+34.6932=39.2932 cal
So,Gross CV of Rice Straw: [3100(0.02+0.018)-39.2932]/1.01245=**77.54 cal/gm**

Water Equiv of the cal meter =3100gm(given).

Experimental Set-up for AD Process and Procedure

The plug flow reactor model (PFR, sometimes called continuous tubular reactor, CSTR, or piston flow reactors) is a model used to describe chemical reactions in continuous, flowing systems of cylindrical geometry.

Materials and Method:

Sample Collection and Preparation:

The sample is collected and prepared after drying and cutting in the Hot Air Oven.After sufficient drying, dry biomass has been graded and sorted to prevent inclusion of unwanted and possible contaminant materials e.g: Detergent,Sand,Dirt etc.

Inoculum Preparation

Fresh CM slurry has been used as inoculum in this study, as it contains all the required

groups of microbial consortium essential for AD Process.

Alkali Pretreatment

Alkali Pretreatment. Alkali pretreatment involves the use of alkaline solutions using KOH,to remove lignin and a part of the hemicelluloses by destroying the links of lignin and other polymers.

Set up of Test Reactor:Before charging in PFR,Sample is charged in a Test Reactor.It consists of a completely randomized arrangement of bench top batch reactors in a 3 × 3 replicated laboratory experiment and has been conducted in a series of 3 laboratory aspirator bottles made of borosilicate glass of 500 mL capacity each. Rubber cork has been fitted tightly to the neck of each bottle to help maintain the anaerobic environment. Three glass tubes made of borosilicate glass have been fitted to rubber cork tightly. Each glass tube consisted of a glass knob or valve at the opening end. Among three tubes one of them has been used as gas delivery tube and the other two have been kept dipped in slurry, one for sampling out from time to time for determination of pH, total solid, and volatile solid.

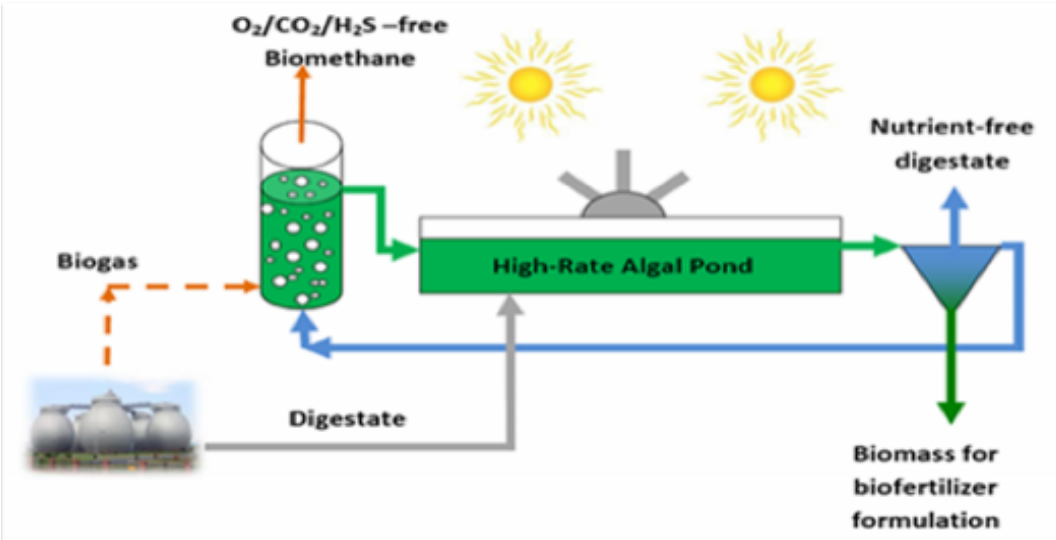


Fig 8:Schematic diagram of Biogas Process[50]

Experimental Procedure

It consists of a completely randomized arrangement of bench top batch reactors in a 3 × 3 replicated laboratory experiment and has been conducted in a series of 3 laboratory aspirator bottles made of borosilicate glass of 500 mL capacity each. Rubber cork has been fitted tightly to the neck of each bottle to help maintain the anaerobic environment. Four glass tubes(Gas Pipe) made of borosilicate glass have

Fig 9:Exp.Set-up of PFR(Plug Flow Reactor)

been fitted to rubber cork tightly. Each glass tube consisted of a glass knob or valve at the opening end. Among three tubes one of them has been used as gas delivery tube and the other two have been kept dipped in slurry, one for sampling out from time to time for determination of pH, total solid, and volatile solid. A cylindrical jar essentially fitted with glass knobs or valves at both ends, made of borosilicate glass and with 500mL capacity of bottle , has been used for measuring biogas by water displacement method. The gas delivery tube has been connected to one end of the jar by means of rubber tube. Similarly the other end of the tube has been connected to a glass jar of 500mL capacity to facilitate the volume of displaced water upon commencement of biogas into the jar. The Digestion process is carried out following the Loading Rate with respect no of days.

Setup of Biogas Measurement

In order to prevent the dissolution of biogas into water, brine solution has been prepared and used to measure yield of biogas by displacement of water.Each bottle is poured with measured water of 456.25ml and blocked the head with rubber cork and stick with plaster of Paris.The gas is measured after the interval of 24hs.

The research work has been carried out in order to study the influence of Alkaline pretreatment on the kinetics of biogas synthesis. Exhaustive investigations with Alkaline Pretreatment of wastes have been carried out at room temperatures for 40 days.Thereafter the pretreated materials have been charged for AD. Biogas production rate and cumulative biogas production have been plotted against hydraulic retention time.

Results & Discussion

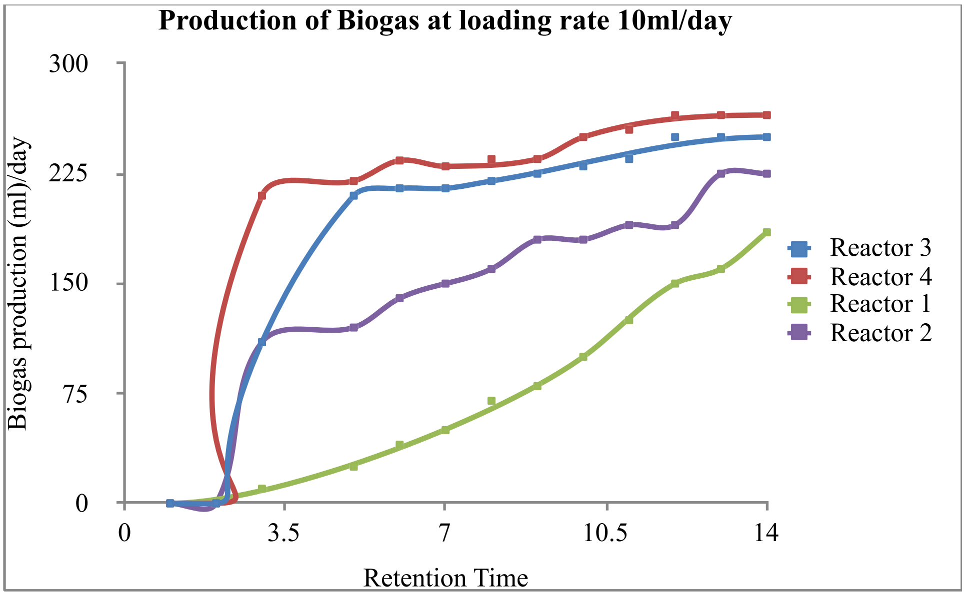


Fig10: Biogas prod Vs RetentionTime

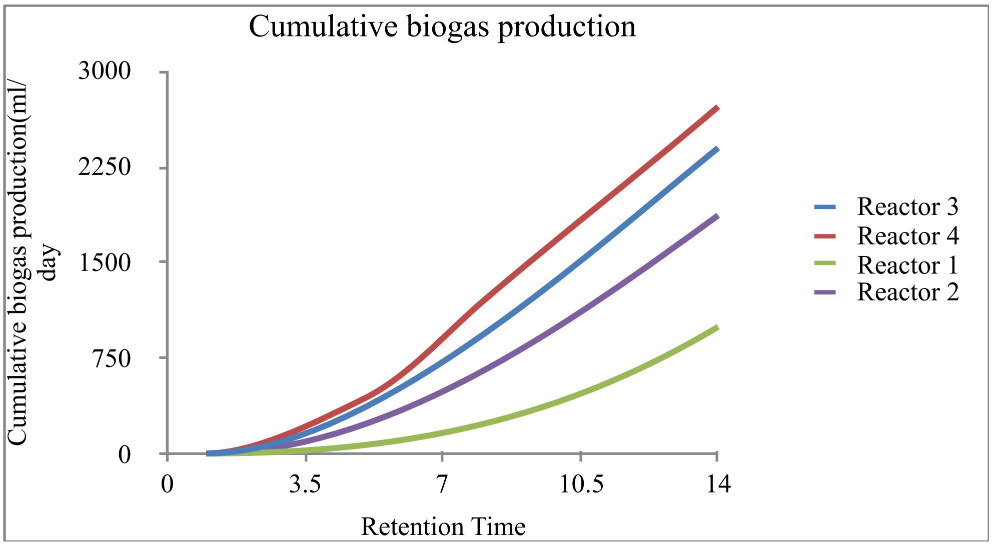


Fig11: Cumulative Biogas prod Vs RetentionTime

The above Figure shows shows the different kinetics for the different loading rate run in the reactors.

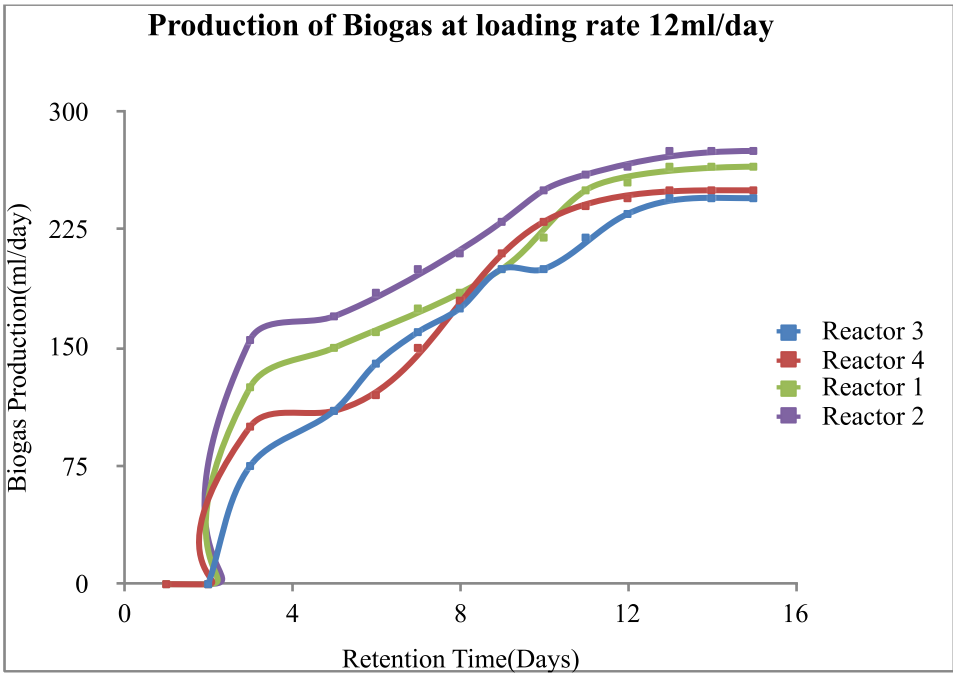


Fig12: Biogas prod Vs Retention Time

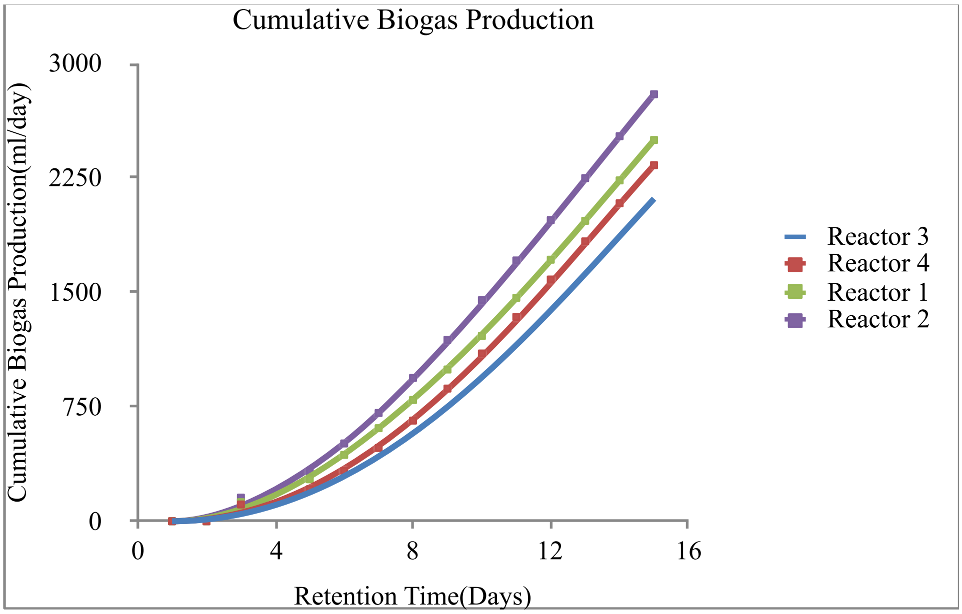


Fig13:Cumulative Biogas prod Vs Retention Time

The above Figure shows shows the different kinetics for the different loading rate run in the reactors.

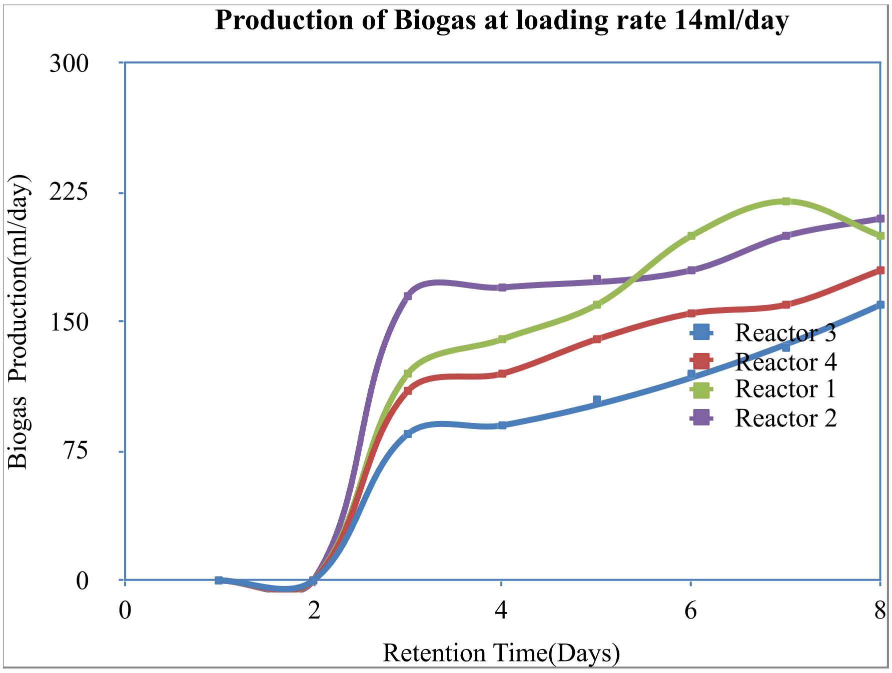


Fig14:Biogas prod Vs Retention Time

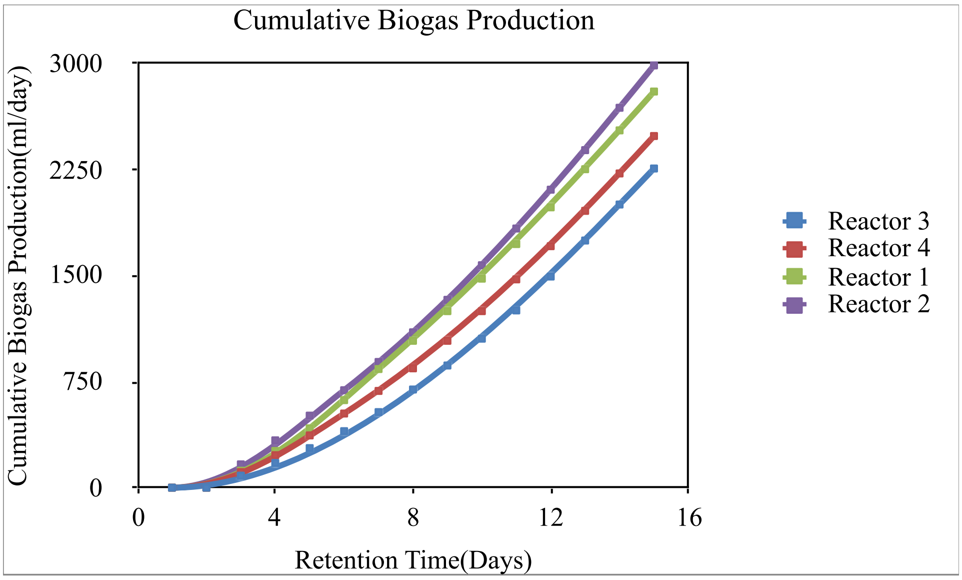


Fig15:Cumulative Biogas prod Vs Retention Time

Anerobic Digestion for Pretreated Rice Straw by PFR(Plug Flow Reactor):

Anaerobic digestion is a natural biological process when bacteria break down organic matter in environments with little or no oxygen. A controlled enclosed version of the anaerobic breakdown of organic waste is a landfill process which releases methane as one of end products. Several research groups have shown that the AD process can be split into three main stages: *Hydrolysis,Acidogenesis,Acetogenesis,Methanognesis.*

This Process is carried out in PFR(Plug Flow Reactor) as a digester with four volume bottles.The PFR is charged with measured Tap Water and with measured Pre-Treated Rice Straw for 40days approx at a Particular innoculum concentration provided in each bottle at three different loading Rate 10ml,12ml and 14ml/day respectively.

As we know,The PFR model works well for many fluids: liquids, gases, and slurries. Although turbulent flow and axial diffusion cause a degree of mixing in the axial direction in real reactors, the PFR model is appropriate when these effects are sufficiently small that they can be ignored.

We get the High yield of biogas using PFR for disgetion.

Table:6

Reactors	**Length of the Reactor**	**Loading Rate(ml/day)**
Reactor 1	6inch	10ml,12ml,14ml
Reactor 2	12inch	10ml,12ml,14ml
Reactor 3	18inch	10ml,12ml,14ml
Reactor 4	24inch	10ml,12ml,14ml

Since we know PFR is a Tubular Reactor so total length of 24inch is measured. Total length Taken:24inch. So, The tenth of each reactor is 6inch(Reactor 1), 12inch(Reactor 2), 18inch(Reactor 3) and 24inch(Reactor 4) Respectively.

FTIR Analysis for the Sample:

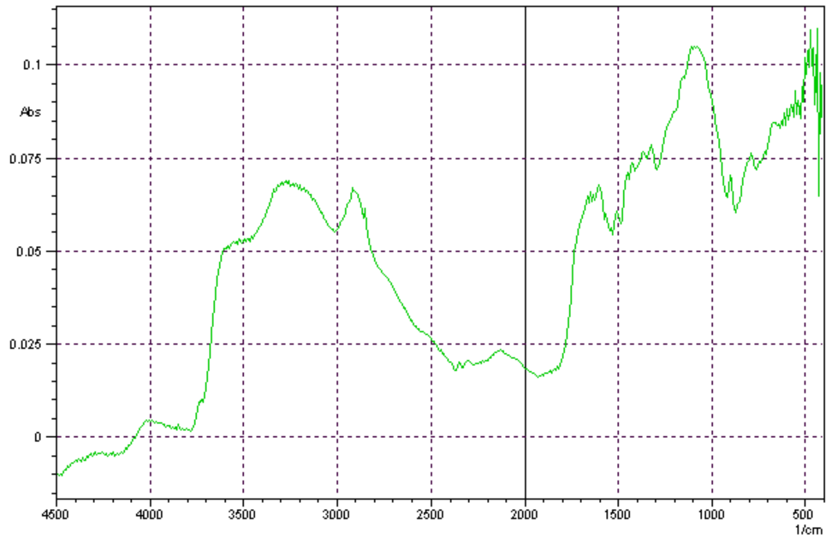


Fig16:FTIR Analysis for Pretreated Rice Straw

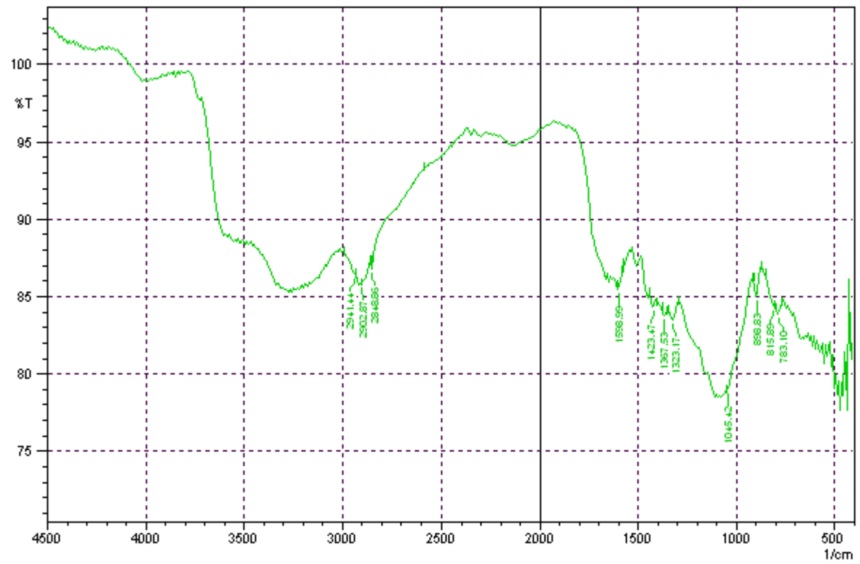


Fig17:FTIR Analysis for Untreated Rice Straw

XRD Analysis for the Sample:

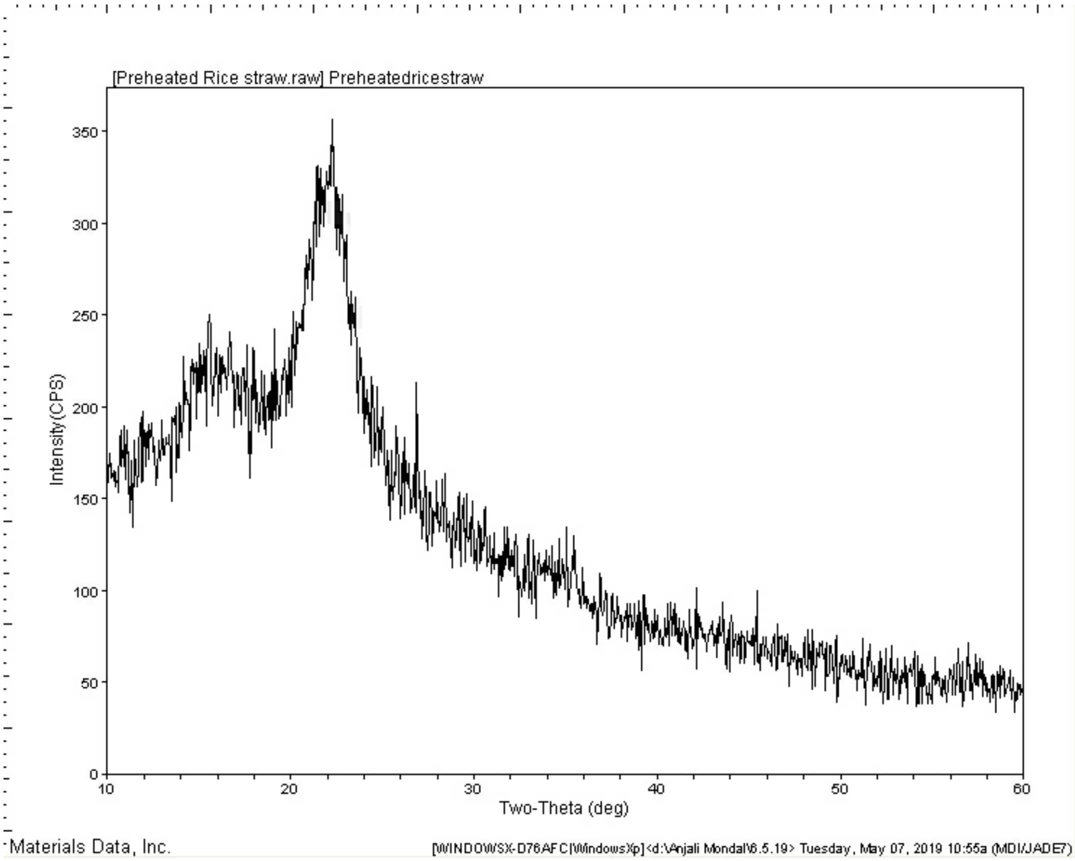


Fig18:XRD Analysis for the Pretreated rice Straw

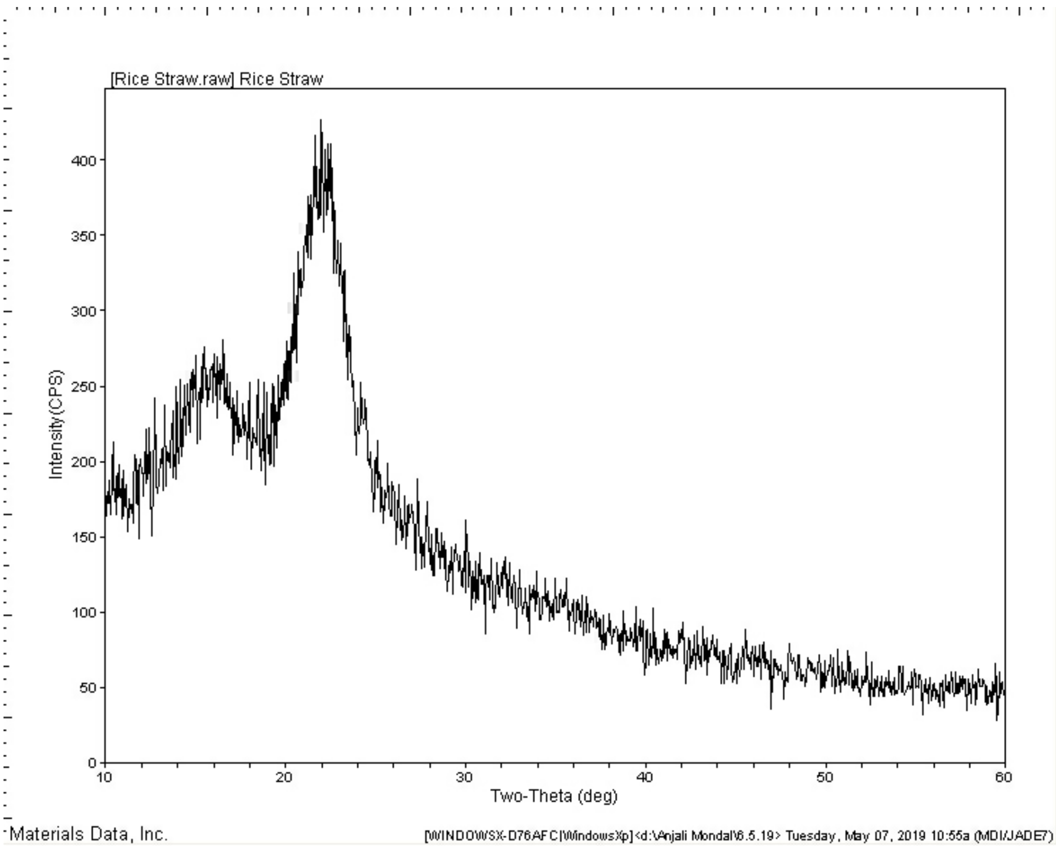


Fig19:XRD Analysis for the Unetreated rice Straw

SEM analysis for the Sample:

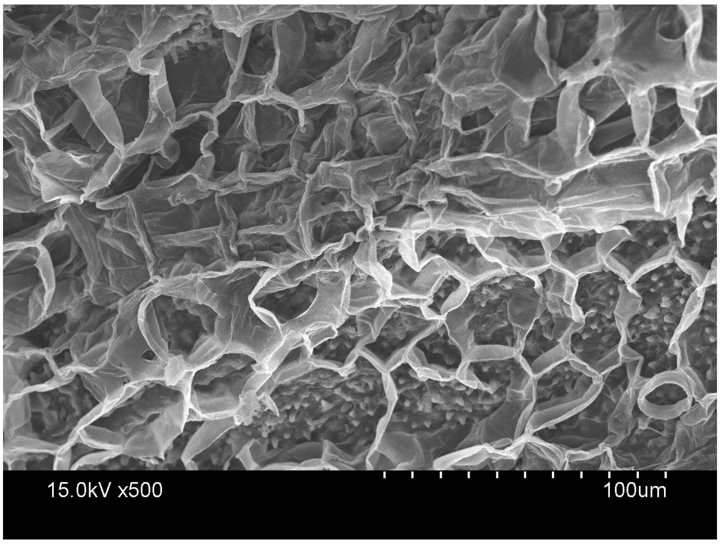
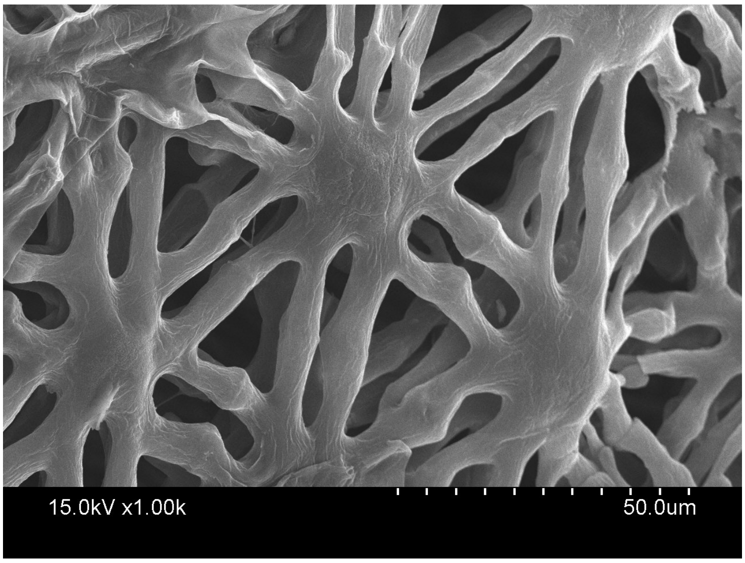


Fig20 and 21: SEM for Pretreated Rice fibrous structure



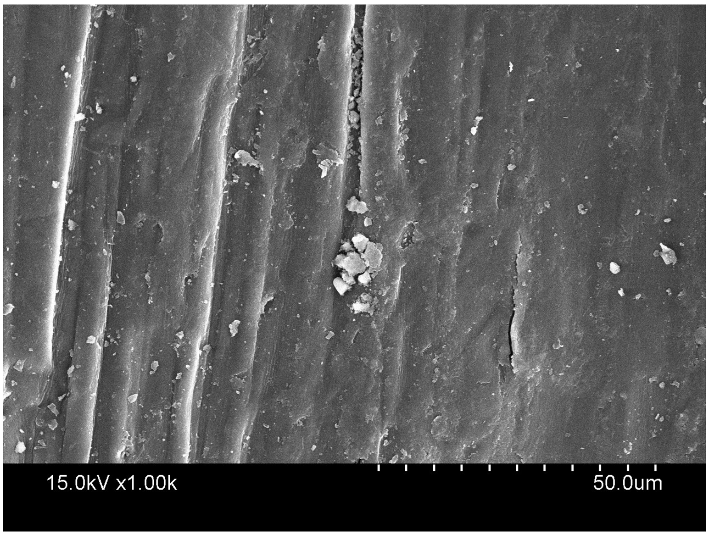
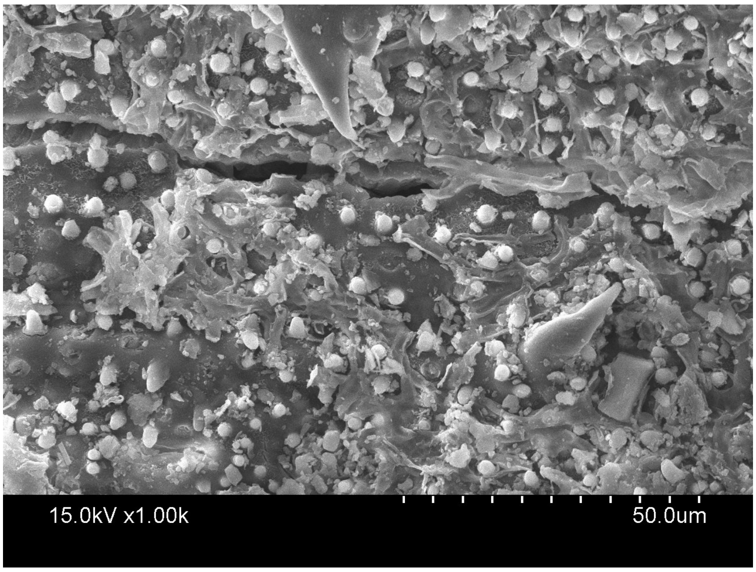


Fig22:<u>SEM For the Untreated Rice Straw Planner Structure</u>



<u>Fig23:SEM For the Untreated Rice Straw</u>

1.Pretreatment

The Process is done under Alkaline Pretreatment of untreated Rice straw at room temperature and 3.5-4hrs of continuous stirring.

This Process is followed to extract the lignin from the untreated biomass to get higher yield of biogas Production for higher accessibility and to make the process and further stages more effective .

Biomass Yield: 30.5*100/50=61%
After Pre-Treatment the Total Biomass taken is Reduced to 61%.

2.Estimation Of Lignin

The method lignin estimation is carried out to extract the lignin from the lignocellulosic biomass for the higher biodegradation to enhance the Biogas production.The lignin is decreased from 12% of Untreated Rice Straw to 9% of Pre- Treated Rice Straw for the higher biodegradability.

3.Calorific value of the Biomass:

The Gross calorific value ,the study shows how the very simplified correlations based on the calculation of carbon and hydrogen content have performances that are similar to those of more complex ones based on the greater number of parameters. The Coolinng applying Dickinson formula: V1(Ta-To)+V2(Tn-Ta), We got the GCV(Gross Cal.Value)=**77.54cal/gm**

We can find out the Performance of Carbon(C) and Hydrogen(H) in the lignocellulosic biomass, calculating the GCV(Gross Cal.Value of the Sample).

Conclusions

The study proposes a better and efficient design of biogas which is suitable for using in houses and canteen. The biogas plant has been planned for easy usage since the maintenance of the plant is low. The PFR biogas plant thus designed has some good features like, 1. The plant can be used in compact spaces and also transportation is easy. 2. It is easy to use and maintain since there are very less moving parts. 3. The slurry in this plant need not be stirred regularly. 4. The biogas is produced regularly in this plant. 5. Since the plant is made of fiberglass, the corrosion does not take place and this increases the life of the plant.

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APPENDIX:

Experimental Tables:

Raw Data of the Biogas production

Table:1 & Table:2 for Loading rate at10ml/day

Day	R1	R2	R3	R4
1	0	0	0	0
2	0	0	0	0
3	110	210	10	110
5	210	220	25	120
6	215	234	40	140
7	215	230	50	150
8	220	235	70	160
9	225	235	80	180
10	230	250	100	180
11	235	255	125	190
12	250	265	150	190
13	250	265	160	225
14	250	265	185	225
	250	235	185	190

Day	R1	R2	R3	R4
1	110	105	150	200
2	320	355	360	405
	555	610	605	630
3	805	845	860	780
4	1010	1075	1115	970
5	1225	1325	1265	1185
6	1455	1590	1435	1410
7	1690	1855	1635	1640
8	1915	2085	1670	1820
9	2140	2315	1845	2005
10	2365	2545	2005	2190
11	2590	2780	2190	2380

Cumulative Values of the Gas

Table:3 & Table:4 for Loading rate at12ml/day

Day	R1	R2	R3	R4
1		0	0	0
2	0	0	0	0
3	75	100	125	155
5	110	110	150	170
6	140	120	160	185
7	160	150	175	200
8	175	180	185	210
9	200	210	200	230
10	200	230	220	250
11	220	240	250	260
12	235	245	255	265
13	245	250	265	275
14	245	250	265	275
15	245	250	265	275

Day	R1	R2	R3	R4
1	0	0	0	0
2	0	0	0	0
3	75	110	125	155
4	185	210	275	325
5	295	330	435	510
6	435	480	610	710
7	595	660	795	940
8	770	870	995	1190
9	970	1100	1215	1450
10	1170	1340	1465	1710
11	1390	1585	1715	1975
12	1625	1835	1970	2250
13	1870	2085	2235	2525
14	2115	2335	2500	2800

Cumulative Values of the Gas

Table:5 & Table:6 for Loading rate at14ml/day

Day	R1	R2	R3	R4
1	0	0	0	0
2	0	0	0	0
3	85	110	120	165
4	90	120	140	170
5	105	140	160	175
6	120	155	200	180
7	135	160	220	200
8	160	180	200	210
9	170	195	210	230
10	190	210	230	245
11	200	225	245	260
12	220	235	260	275
13	240	250	270	280
14	255	265	275	300
15	255	265	275	300

Days	R1	R2	R3	R4
1	0	0	0	0
2	0	0	0	0
3	85	110	120	165
4	175	230	260	335
5	280	370	420	510
6	400	525	620	690
7	535	685	840	890
8	695	845	1040	1100
9	865	1040	1250	1330
10	1055	1250	1480	1575
11	1255	1475	1725	1835
12	1495	1710	1985	2110
13	1750	1960	2255	2390
14	2005	2225	2530	2690
15	2260	2490	2805	2990

Cumulative Values of the Gas