EFFECT OF VARYING ORGANIC LOADING RATE ON BIO HYDROGEN PRODUCTION FROM FOOD WASTE IN A SEMI CONTINUOUS REACTOR

By

Fouzia Rafi

Rabeia Malik

Ibrahim Atique

Ahmad Kamal

Supervisor

Dr. Zeshan

Institute of Environmental Sciences and Engineering (IESE)

School of Civil and Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST), Islamabad

May 2019

EFFECT OF VARYING ORGANIC LOADING RATE ON BIO HYDROGEN PRODUCTION FROM FOOD WASTE IN A SEMI CONTINUOUS REACTOR

A thesis submitted to the
National University of Sciences and Technology
in partial fulfillment of the requirements
for the degree of bachelors of engineering in
Environmental Engineering

By

Fouzia Rafi	NUST-2015-127206
Rabeia Malik	NUST-2015-124446
Ibrahim Atique	NUST-2015-126518
Ahmad Kamal	NUST-2015-133300

Supervisor
Dr. Zeshan

Institute of Environmental Sciences and Engineering (IESE)
School of Civil and Environmental Engineering (SCEE)
National University of Sciences and Technology (NUST), Islamabad

May 2019

APPROVAL SHEET

This is to certify that the Research work described in this thesis is the original work of author(s) and has been carried out under my direct supervision. I have personally gone through all the data/results/materials reported in the manuscript and certify their correctness/authenticity. I further certify that the material included in this thesis is not plagiarized and has not been used in part or full in a manuscript already submitted or in the process of submission in partial/complete fulfillment of the award of any other degree from any institution. I also certify that the thesis has been prepared under my supervision according to the prescribed format and I endorse its evaluation for the award of Bachelors of Engineering in Environmental Engineering Degree through the official procedures of the Institute.

____

Dr. Zeshan
Supervisor
IESE, SCEE, NUST

____

Dr. Zeeshan Ali Khan
HOD Environmental Engineering
IESE, SCEE, NUST

____

Dr. Imran Hashm
Associate Dean
IESE, SCEE, NUST

Acknowledgements

To start with, we are grateful to our respectable supervisor Dr. Zeshan form Institute of Environmental Sciences and Engineering, for his guidance, support and keen interest that made this project achieve success and recognition. Without his mentorship this project would have not been able to achieve its successful completion.

We owe heartiest gratitude to Sir Amir for his moral and technical support with experimental techniques and equipment in the Wastewater lab Institute of Environmental Sciences and Engineering throughout the experimentation phase of this study. His encouragement, support, guidance has paved a way to success for this project.

We wish to present our gratitude to Mr. Basharat for his technical support in the Chemistry Lab of Institute of Environmental Sciences and Engineering. His help with chemicals and experimental procedures has played a major part in successful completion of this project.

Also, we are grateful to our families, friends, and colleagues for their unhindered support and continued motivation that kept us pushing and provided us with the energy to overcome the obstacles in the way.

Abstract

Pakistan is a country with a population of 204.2 million. Being the 6th most populated country there is a lot of consumerism and with it a great deal of waste being generated. Currently there is no proper mechanism for treatment and proper disposal of waste and open dumping leads to a whole new set of environmental problems including emissions of GHGs such as CO2 and CH4. Additionally, Pakistan is also on the verge of energy crisis. 61.8% of the total energy demand of Pakistan is derived from fossil fuels. This high dependence on a depleting source of energy is the major force driving the exploration of renewable energy resources. This study provides an innovative solution to both of the major problems highlighted above in the form of biological production of Hydrogen. Hydrogen is a valuable gas that can be used as a clean source of energy Biological hydrogen production appears to be very promising as it is a non-polluting process and hydrogen can be produced from a wide variety of biodegradable such as Food waste. Dark Fermentation is a biological process for hydrogen production showing highest potentials for sustainable hydrogen production, because of its independency on light and the possibility of using a range of different organic substrates. The efficiency of this process can be improved by pre-treatment of the organic substrate in order to screen the microbial diversity. Besides all the advantages of Biohydrogen production from Dark Fermentation it is challenged by low molar yield, large reactor size and high cost in upscaling to industrial scale. This study reports a research on increasing volumetric hydrogen production rates (VHPR) by varying organic loading rates (OLR) in Continuously Stirred Tank reactor of 13 L. The OLR values of 25, 33 and 50 gVS/L/d with hydraulic retention time of 24, 18 and 12 h respectively were investigated. Under thermophilic conditions with a pH of 5.5, maximum VHPR of about 1LH_2/L/d was observed at an OLR of 33 gVS/L/d. Hydrogen yield also showed an increasing trend to a certain point with increasing OLR and was found maximum at 33 gVS/L/d.

Keywords: Biohydrogen, Dark Fermentation, Continuously Stirred Tank Reactor, Organic Loading Rate, Volumetric Hydrogen Production Rate

TABLE OF CONTENTS

List of Tables

List of Figures

ABBREVIATIONS

VS	Volatile Solids
TS	Total solids
COD	Chemical Oxygen Demand
TOC	Total Organic Carbon
VHPR	Volumetric Hydrogen Production Rate
YH_2	Hydrogen yield
HRT	Hydraulic Retention Time
CO_2	Carbon Dioxide
TKN	Total Kjeldahl Nitrogen
L	Liter
VFA’s	Volatile Fatty Acids
Mg	Milligram
C/N ratio	Carbon Nitrogen Ratio
%	Percentage
^0C	Degree Celsius
d	Day

Chapter 1

INTRODUCTION

1.1 Background

Every year, the energy demand of Pakistan goes on increasing because of a number of reasons including but not limited to alarming increase in population and industrialization. The major indicator for the crisis is frequent outages of power which further links to the economic downfall of the country. With fossil fuels depleting at a high rate, the cost of energy required to fulfill basic needs of everyday life has increased.

Moreover, organic fraction of Solid Waste has a great potential to be used as substrate in biological processes since it is biodegradable, easily available and cheap.

Thus, focusing on the SGD 7 that states “Ensure access to affordable, reliable, sustainable and modern energy for all” and SDG 12 “Sustainable consumption and production” our main objective is to work out a viable solution to combat energy crisis by shifting to more cleaner production ways and to make essential energy more affordable by using waste as a source of energy.

1.2 Magnitude of Problem

Total energy derived from fossil fuels in Pakistan is 146.10 billion kWh. Whereas the energy derived from renewable sources is only 16.5 billion kWh which constitute 7% to the total energy production of Pakistan. This high dependence on a depleting source of energy creates a lot of environmental concerns and is the major force driving the exploration of renewable energy resources.

130,293 tons of waste is generated in Pakistan every day. MSW generation rate in Pakistan is 0.5-0.6 kg/person/day. Out of this 50-60% is organic and biodegradable in nature. Improper disposal of this waste causes Gaseous emissions, Water pollution through leachate and surface runoff, Soil pollution and Disease transmission by nurturing vectors.

This present situation can be improved by employing waste to energy technologies that ensures a contribution in managing waste along with shifting dependence on renewable energy sources.

1.3 Hydrogen: A Potential Solution

Hydrogen is a clean source of energy and holds a substantial contribution towards the future of renewable energy sources because of its high energy content, it is 2.75 times higher than hydrocarbon fuel. Hydrogen upon combustion produces clean water. It can be used as an alternative fuel for transportation because it is easier to carry and can be used directly in fuel cells. On top of that, shifting to hydrogen enables the country to lower its carbon emission and subsequently earning carbon credits.

1.4 Research Motivation

- Present situation of energy crisis in Pakistan
- Open dumping of organic waste

Pakistan has a potential to combat energy crisis as well as means to reduce its carbon footprint. Negligence has made the situation only worse thus this research has been conducted with a purpose to explore possible means to meet the energy demands in most environmentally friendly ways as possible.

Furthermore, availability of Food Waste in abundance and its potential to be used as substrate for energy production added to the viability of Biological Hydrogen Production.

1.5 Problem Statement

Hydrogen production from biological processes is very attractive but it is challenged by

- Low Molar Yields
- High Cost
- Larger Reactor Size

These challenges associated with Hydrogen production are the main hurdles in its industrial acceptability. Thus, more attention should be paid to increase Volumetric Hydrogen Production Rates by varying Organic Loading Rates.

Higher the OLR, smaller the size reactor needed for process and therefore lower the cost of reactor

1.6 Objectives

Our main objective is to make Hydrogen an attractive solution by making its production economically feasible, environmentally friendly and industrially applicable.

Considering the challenges faced in up-scaling bio hydrogen production, the main objectives of this study are:

1. Design, procurement and operation of a semi-pilot scale continuously stirred tank reactor (CSTR) for Bio hydrogen production
2. Optimization of Organic Loading Rate in order to obtain maximum Volumetric Hydrogen Production Rate.

1.7 Existing Solutions

Hydrogen is produced on industrial scale by several methods like Steam Reforming of natural gas, Gasification, Water Electrolysis etc. These processes are extremely energy intensive and use nonrenewable energy sources making hydrogen production expensive. Hydrogen production from these methods have a huge carbon footprint which is environmentally unacceptable.

On the other hand, biological methods like Dark Fermentation offer a cost effective and environmentally friendly method for bio hydrogen production.

1.8 Introduction to Dark Fermentation

Dark fermentation is a process that uses fermentative bacteria for hydrogen production. It is preferred over other biological processes because it is faster and has several advantages like no light dependency, high production rates and it can use various organic wastes as substrate. Dark fermentation involves biological conversion of the complex organics such as fats, proteins and carbohydrates in to simple organic materials in the first stage and subsequent stabilization in the following stages.

Chapter 2

LITERATURE REVIEW

2.1 Background

Annually Pakistan generates 1.3 billion tons of municipal solid waste and this is expected to increase to approximately 2.2 billion tons per year. Out of this MSW produced annually, 30% is food waste. This large fraction of waste is mainly generated due to lack of urban planning, inadequate waste management equipment, lack of awareness and education. Food waste has both environmental and economic value. This waste is recklessly dumped in open streets or disposed in landfill. Once anaerobic conditions prevail in the landfill it becomes a source of gases like Methane and Carbon Dioxide. This problem can be catered by realizing the potential of food waste as an asset and using it to fill the energy deficit. Controlled digestion of this organic waste to produce energy is presented as one possible solution.

2.1.1 Anaerobic Digestion

Anaerobic Digestion is a combination of processes involving microorganism activity in order to break down biodegradable organic material in complete absence of oxygen. This process is universally known and accepted for the production of biogas from suitable substrates. The process is known to occur where ever anaerobic condition prevails and organic biodegradable material is present for example in stomachs of humans to the landfills. The anaerobic process has four steps Hydrolysis, Acidogenesis, Acetogenesis and Methanogenesis in order. The first two steps are the key for hydrogen production and hydrogen production starts initially with the help of Hydrogen formers. In Acetogenesis and Methanogenesis, the last two steps of the anaerobic digestion, the hydrogen is consumed by methanogens and acidogens for the production of methane.

Biohydrogen, in this process, is produced by inhibiting the last two steps by maintaining pH, temperature, treating inoculum and providing high organic loading rate which inhibit the activity of the hydrogen consumers. The activity of methanogens can be ceased by maintaining the pH at a value of 5.5 which has been proved to be the optimum pH for the production of Biohydrogen. So, at this pH no amount of hydrogen will be consumed by the methanogens.

At HRT of 2.9 days, Temperature 55 ºC and pH 5.5, biohydrogen produced from food waste had a yield of 147,300 L/kg and a productivity of 51,324 L/kg/d (Venegas, 2015).

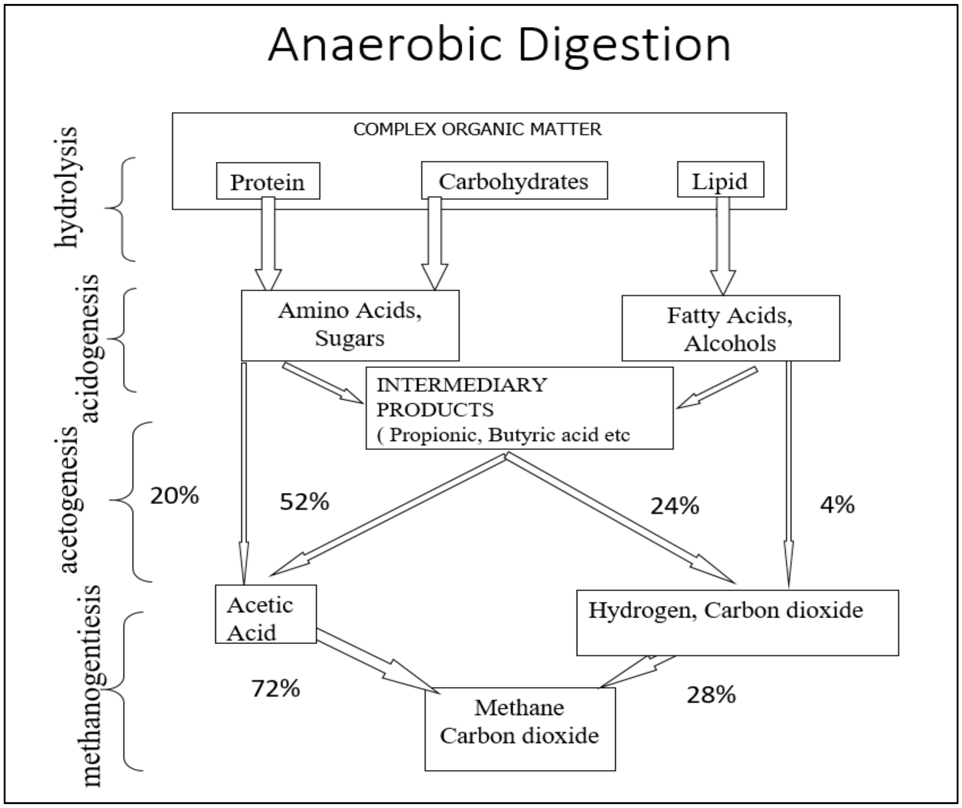


Figure 2.1 Anaerobic Digestion Process

2.1.2 Methods for Biohydrogen Production

Hydrogen can be produced from a number of methods but the three major biological methods for biohydrogen production are given below:

- Photo fermentation
- Dark fermentation
- Combined fermentation

The table on the next page is a Comparison of the above three mentioned processes in terms of advantages and disadvantages.

Table 2-1 Comparison of processes used for Biohydrogen Production

Dark Fermentation	**Photo Fermentation**	**Combined Process**
	Advantages	
i. Economical ii. No external light source required iii. Hydrogen evolution rate is higher than other processes iv. Production of carbon rich metabolites and CO_2 occurs which can be removed or separated from H_2, sequentially stored in biomass or converted to other substances, such as CH_4 v. Microbes involved are spore formers and hence can function on higher temperatures	i. Natural sunlight and biomass are used ii. Natural photo-synthetic bacteria are used for productive activity iii. Higher yield of H_2 than dark fermentation iv. Good for large-scale purposes	i. Both light and dark fermentation bacteria are used ii. Faster hydrogen formation iii. Higher hydrogen productivities iv. Lesser Volatile Fatty Acids (VFAs) formation than dark fermentation v. The time required by Combined Fermentation to reached finality of fermentation process is 6 days. Lesser than both Dark and Light fermentation when achieved separately.
	Disadvantages	
i. Low yield of H_2 per substrate consumed due to	i. Complex nutritional requirements of the Rhodobacter species	i. Inhibitions caused by high concentrations of VFAs and NH_4-N

metabolic fundamentals ii. Low efficiency of the process	ii. Continuous light source required iii. Expensive for large-scale purposes iv. Strict control requirements for environmental conditions: • T = 30–35°C • pH = 6.8–7.5 v. Inhibitions caused by high concentrations of VFAs (>2500 mg L^{-1}) and NH4-N (>50 mg L^{-1})	ii. Severe control of physico-chemical conditions iii. The medium used to grow bacterial species is dark fermentation's effluent, it needs complex nutritional added

2.1.3 Reactors for Biohydrogen Production

Bioreactor configuration is of prime importance in hydrogen production. Bioreactors are specific to the type of fermentation process that is being carried out. It is the type of reactor that determines the microenvironment inside the reactor, prevailing microorganisms' population, contact time and face to face interaction of inoculum and substrate. For research purposes usually batch reactors are used as they are easy to operate and flexible in their operations. Most commonly for continuous operation Continuously Stirred Tank Reactor (CSTR) is used. A CSTR is preferred because of its high up-scaling potential. It is considered as the most economical option better than others.

Comparison of some of the Reactors used for biohydrogen production is is given in the table 2.2:

Table 2-2 Comparison of Reactors used for Biohydrogen Production

Continuously stirred Tank Reactor (CSTR)	Upflow anaerobic sludge blanket (UASB)	Anaerobic fluidized bed reactor (AFBR)	Anaerobic packed bed reactor (APBR)
Advantages			
• Simple in construction • Easy to operate • Effective stirring prevents formation of dead zones • Provides good contact between the substrate and microorganisms • Small HRT can be maintained which is favorable for hydrogen production	• Microbiological granules are formed on the gas/liquid/gas separator on top of the reactor • Active biomass sediments for a thick biomass blanked zone at the bottom • Between these two highly active sheets of biomass the process of hydrogen production takes place with greater efficiency	• Characterized by good mixing • Good retention of biomass • High hydrogen production efficiency at low HRTs and high biomass concentration • The kind of support material and microorganism immobilization type has an important influence on efficiency	• Good retention of biomass in the reactor
Disadvantages			
• Biomass concentration is sometimes washed out in too short HRTs • Low retention of biomass	• Long start-up period i.e. the time necessary to form large granules is approximately 5 months	• Energy is required for fluidization of bed • Excessive shear stress can	• Higher mass transfer resistance • Low substrate conversion rate • Low hydrogen production rate

		detach the biomass	• Severe clogging issue

2.2 Comparison Studies

As compared to the lipid, protein and cellulose components, the carbohydrate fraction in food waste plays an important role in the hydrolysis step during anaerobic degradation. The only inhibition factor is the fat content which can be reduced by appointing a filtration mechanism (Yasin et al. 2013)

According to Kumar (2018) Dark fermentation is an excellent avenue for biohydrogen production compared to other biological systems.

Lee et al. (2008) evaluated the performance of CSTR with a stirring speed of 160 rpm for thermophilic temperature (55^{O}C) at two different VLR (19g-COD L^{-1} day^{-1} and 28g-COD L^{-1} day^{-1}). The best performance in terms of HPR (L-H_2 $L^{-1}day^{-1}$) was obtained at 28 g-COD L^{-1} day^{-1} with a HPR of 1L-H_2 L^{-1} $day^{-1.}$ Increasing the VLR from 19 to 28 not only increased HPR but also increased BioH_2 concentration in the biogas from 35% to 48%.

When subjected to temporary shock loading, the productivity of biohydrogen in a continuous reactor was increased (Monry et al. (2017). At maintained pH of 5.5, thermally pretreated anaerobic sludge and glucose were employed in 2 CSTRs, each Reactor was subjected to four organic shock loads (two at HRT = 5 h, OLR = 102.7 g COD/L-d during 6 and 24 h, respectively, and two at HRT = 3 h, OLR = 171.2 g COD/L-d with the same duration). H_2 productivity was improved by the temporary organic shock loads, increasing the HPR up to 40%.

2.3 Findings

The major findings of the comparison studies were the following:

2.3.1 Food Waste: A Potential Substrate

With increasing energy demand globally, utilizing renewable resource such as food waste for biohydrogen production can be a novel and promising approach for substituting fossil fuels and solving waste disposal problem simultaneously. Suitability of substrate for biohydrogen production depends on several physico-chemical parameters.

Physico-chemical characteristics of food waste are very important is designing and operation of an anaerobic system. Food Waste has a good potential to be digested anaerobically as it has a high substrate concentration in term of Carbohydrates ranging from 72 – 85.2 % and

COD 19.3 – 346 g/L. Carbon to Nitrogen (C/N) ratio of Food Waste also lies in the suitable range for biohydrogen production that is between 9 – 21.

2.3.2 Operating Conditions of Bioreactor

In a continuous operation, HRT and pH control the biohydrogen production in many ways. pH is also considered as an important performance indicator. Acidic pH indicates that the process of anaerobic digestion has reached the Acidogenesis stage which is characterized by hydrogen production. Higher pH is suitable for Methane production and hinders the activity of Hydrogen producers. Therefore, optimum pH value for biohydrogen production is between 5 – 6. HRT is characterized by the time microbial cultures are allowed to grow and biodegrade the substrate. Longer HRT favor Methane production as methanogens required longer period of time to grow and prosper. So, at fixed pH, say 5.5, HRT ranging from 6 – 12 is found to be most effective for Hydrogen production. An HRT beyond the lower limit can cause washing out of hydrogen producers

.

2.3.3 Low Molar Yields

Dark Fermentation has been identified as the most trusted process for biohydrogen production. As compared to Photo Fermentation, its independency on light and relatively easy bioreactor requirement makes it attractive. Besides this, Dark Fermentation is challenged by Low Volumetric Yields.

At maintained pH and carefully assigned HRT, the molar yields can be increased by varying the volumetric organic rates. The efficiency of digestion can be noted by VS removal percentage. The rate of hydrogen production shows a dependence on loading rates but increasing the VLR beyond a limit can hinder the production mainly due to fat inhibition.

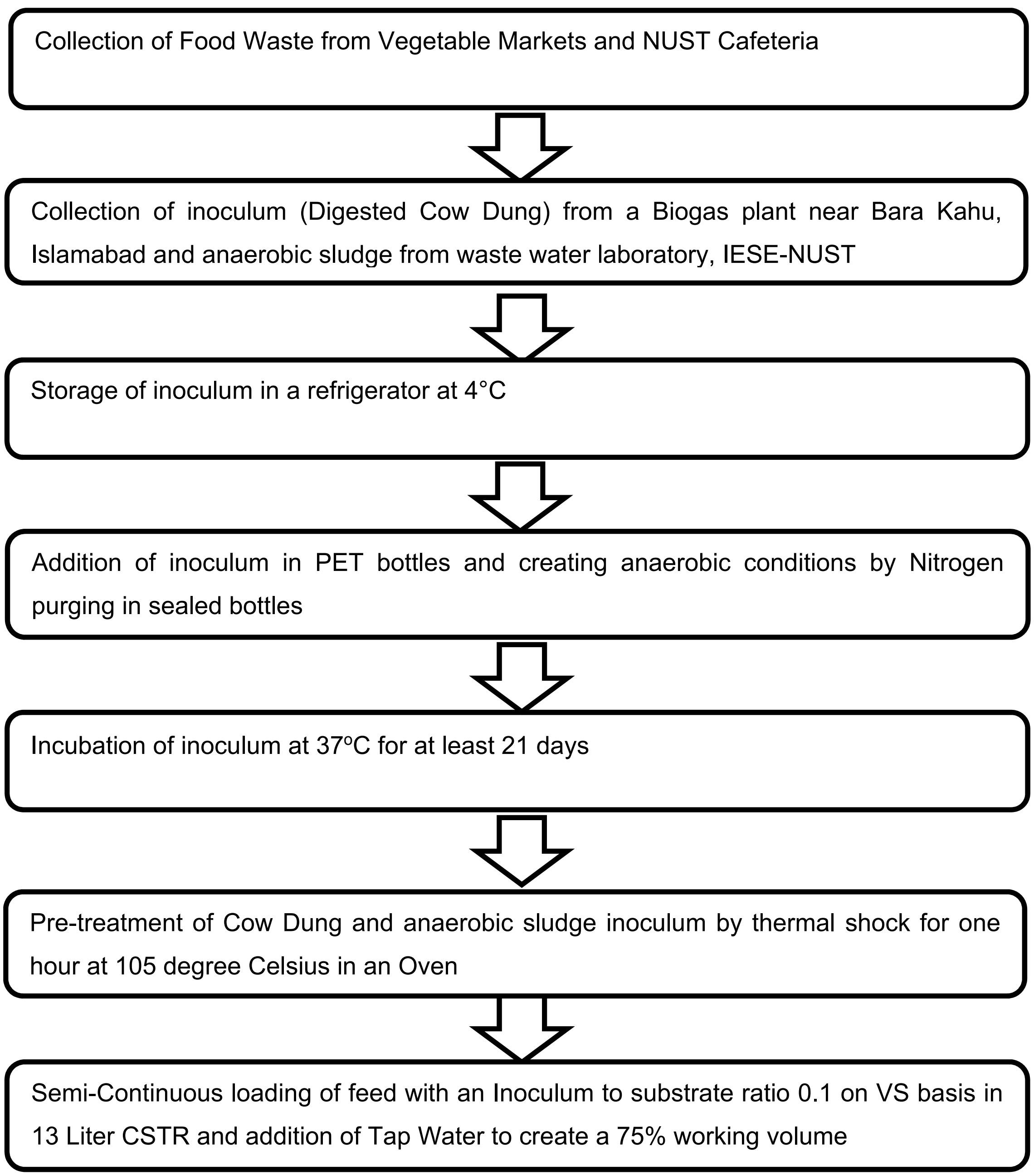
On this basis a problem statement was developed to increase Volumetric Hydrogen Production Rate by varying Organic Loading Rates.

Chapter 3

MATERIALS AND METHODS

In this chapter, the methodology for bio hydrogen production from food waste in a semi continuous reactor will be discussed in detail.

3.1 Process flow diagram for experimental study



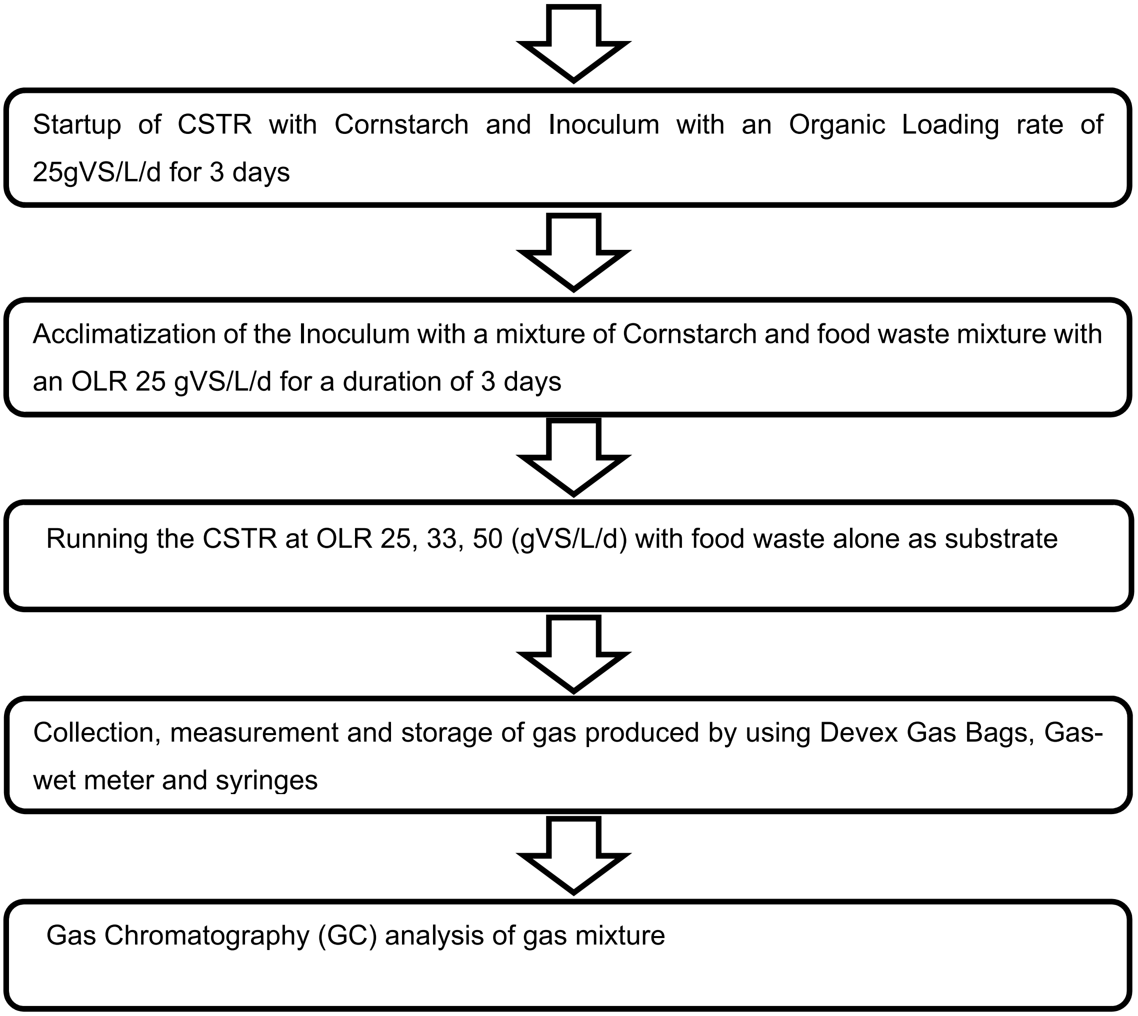


Table 3-1 Flow Chart of Experimental Study

3.2 Substrate Collection and Preparation

The food waste was collected from vegetable market and NUST Hostel Mess. Literature review suggested that organic waste is more suitable for anaerobic digestion as compare to inorganic waste. This is because of the fact that organic waste is easily biodegradable and relatively abundant. In Pakistan Organic waste is nearly 65% of the total waste generated.

3.2.1 Composition of Food Waste

Table 3.2 shows the components used in substrate along with their weight percentages

Table 3-2 Composition of substrate

Components of Substrate	Percentage in total substrate
Lentils	35
Bread	10
Boiled Rice	10
Mixed Vegetable	25
Tomato	20

Based on our literature search the percentage composition was so decided to maintain Optimum Carbon to Nitrogen ratio of 20, as in literature the optimum C/N ratio for bio hydrogen production lies between 20-21.

Lentils are kept in a high percentage as its TKN value is more than the rest of the components. So to avoid the addition of nutrients for microbial activity, lentils have a relatively high percentage which provides sufficient nitrogen.

3.2.2 Shredding and Mixing of Food Waste

The collected waste was shredded manually with knives and graters to reduce the particle size. Shredding was done for easy biodegrading of food waste. All the shredded substrate components were added in the proportions given above and mixed homogenously.

Figure 3.1 Food waste Mixture

3.3 Inoculum Collection and Preparation

Inoculum is a microbe rich media substance that has the ability to initiate the activity of micro-organisms when substrate is available. These microorganisms are responsible in anaerobic digestion for production of biogas.

Some of the Inoculums that can be used for bio hydrogen production are swine wastewater, sewage sludge, animal manure, cow dung etc.

3.3.1 Collection and Storage of Cow Dung

For this project, digested cow dung and anaerobic sludge were used as an inoculum. Digested cow dung was obtained from a biogas plant at Bhara-Kahu. The anaerobic sludge was collected from wastewater lab at IESE. Both the inoculums were stored temporarily at $4^{o}C$ in a refrigerator to keep the microbes alive but relatively inactive.

3.3.2 Sieving of Inoculum

Both the inoculums were sieved separately using a mesh 2mm to remove waste materials and obtain a low-solid inoculum. Sieving is important because efficiency of anaerobic digestion is effected by large particle size.

Figure 3.2 Sieving of Inoculum

3.3.3 Nitrogen Purging and Sealing of Inoculum bottles

Figure 3.3 Nitrogen Cylinder

Once the sieving was done, digested cow dung and anaerobic sludge were both half-filled into two separate 500ml glass bottles. These bottles were closed with rubber septum. The basic purpose of nitrogen purging was to create anaerobic conditions inside the bottles.

A hypodermic needle was inserted into the rubber septum and was connected to the nitrogen cylinder. Another hypodermic needle was placed in the rubber septum for making a way out for air, when nitrogen supply was on. The purging was done for about 5 minutes on each bottle.

3.3.4 Incubation of Inoculum

After nitrogen purging the inoculum bottles were incubated at 37 oC for at least 21 days. Biogas produced in the bottles was discharged daily. Incubation was done for removing any organic content present in the inoculum.

3.4 Inoculum Pre-treatment

The process of anaerobic digestion has four steps Hydrolysis, Acidogenesis, Acetogenesis and methanogenesis. In acetogenesis and methanogenesis hydrogen consuming bacteria like methanogens for methane production consume the hydrogen produced during acidogenesis. For hydrogen to produce methanogens are required to be suppressed.
Based on our literature search it was concluded that heat pretreatment of the inoculum at 90 ^{o}C for 1 hour suppressed the activity and growth of methane producing bacteria and selectively enriched the culture of methane producing bacteria.

3.5 Parameters of Analysis for Food Waste and Inoculum

Food waste and inoculum were characterized for the following parameters

3.5.1 Moisture Content

Substrate and inoculum sample was weighed initially and were placed in an oven at 105 degree centigrade for 18-24 h. After this, the sample was placed in a desiccator for cooling and was weighed then.

$$Moisture\ Content\ (\%) = \frac{\text{Wet weight } - \text{Dry weight}}{\text{wet weight}} \times 100$$

3.5.2 Total Solids (TS)

Total solids of the sample was simply calculated by subtracting Moisture content from a total 100%

Total Solids (%) = 100 – *Moisture Content (%)*

3.5.3 Volatile Solids (VS)

Same dried sample was then placed inside a muffle furnace at 550 degree centigrade for 30 minutes. The difference of both the weights, before and after, gave the volatile solids.

$$Volatile\ Solids\ (\%\ of\ TS) = \frac{\text{Dry weight } - \text{ weight after ignition}}{\text{dry weight}} \times 100$$

3.5.4 Total Organic Carbon (TOC)

Organic carbon were found out by dividing the VS (as % of TS) by 1.8. This conversion factor has been opted by literature search.

$$Total\ Organic\ Carbon\ (\%\ of\ TS) = \frac{VS\ (\%\ of\ TS)}{1.8}$$

3.5.5 Total Kjedhal Nitrogen (TKN)

TKN was found out by digesting the sample with Mercury oxide, potassium sulphate, H_2SO. Distilling it with boric acid and then titrating against 0.1 Normal Sulphuric acid.

$$Total\ kjedhal\ Nitrogen\ (\%\ TS) = \frac{Volumeof\ H2SO4\ used\ \times\ 0.1 \times\ 14}{weight\ of\ sample\ in\ g}$$

3.5.6 C/N ratio

Carbon to nitrogen ratio was found out by simply dividing Total organic carbon (TOC) by Total Kjedhal Nitrogen (TKN).

$$C/N = \frac{TOC}{TKN}$$

Figure 3.4 Inoculum Sample for Characterization

Figure 3.5 Substrate Sample for Characterization

3.6 Experimental Setup

The figure 3.6 shows the process flow diagram of the experimental setup. It has a continuously stirred tank reactor (CSTR) of 13L containing a mixture of substrate, inoculum and water whose pH was maintained at 5.5 by adding buffer solution, was, subjected to nitrogen purging for maintaining anaerobic conditions. A temperature of 550C was maintained by passing heated water through the water jacket surrounding the reactor, using a heating rod and temperature controller. The gas produced during this collected collected in gas collection bags on regular basis. Collected gas was then analyzed by Gas Chromatography (GC) analysis in order to find out the percentage of bio hydrogen in the biogas.

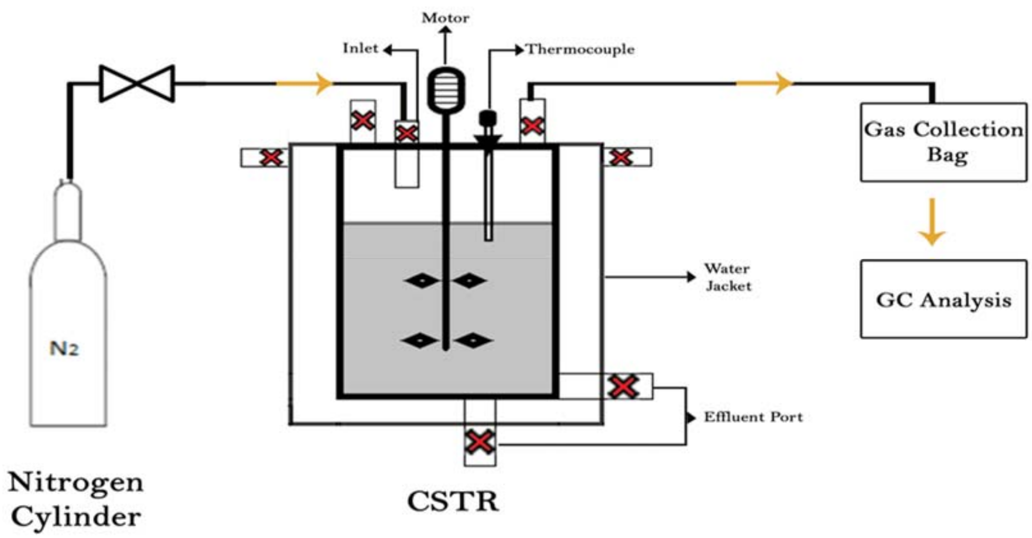


Figure 3.6 Process flow diagram of experimental set-up

3.6.1 Design and construction of CSTR

Stainless steel was used in the construction of reactor as it ensured the uniform heating of contents and that the system was rust proof and leakages development was minimized.

- **Dimensions**

The reactor had total of 13 liters volume while the working volume of the reactor was 10 liters. The rector was cylindrical in shape to facilitate the mixing of substrate and inoculum. The volume is calculated using formula V= π*r^2*l. The diameter and height of the reactor were set in 1:1.5. Keeping the total volume 13 liters the diameter and height were calculated as 8.5 inches and 13 inches respectively.

- **Impeller**

The impeller was designed according to the design considerations found in the literature review. The total diameter of one impeller was kept a half of total diameter of reactor. The distance from bottom of reactor was kept equal to impeller diameter. The spacing between two impellers was also kept equal to one impeller length. The impellers used were Rushton turbines. The diameter of internal plate was kept 2.7 inches. The height of blades was kept equal to total length divided by 5 and the blade width was kept equal to total length divided by 4 i.e. 0.8 and 1 inch respectively.

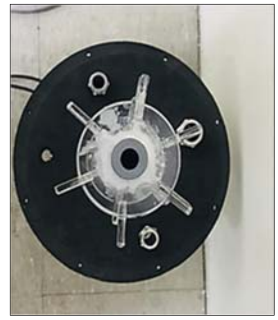


Figure 3.7 Rushton turbine Impeller

- **Water jacket**

The reactor was provided with a water jacket to keep the temperature in control. The temperature suitable for the experiment was 55 degree centigrade. The water jacket had an external source of hot water which was supplied by a temperature control unit. The temperature control unit comprised of immersion heater, temperature controller and a thermocouple which was fitted inside the reactor.

- **Maintaining anaerobic conditions**

For maintaining the anaerobic conditions inside the reactor, the reactor was sealed by tightly nutting the lid. Furthermore, silicon glue was applied to any possible gas leakage sites.
Nitrogen purging was done by connecting the inlet of the reactor through a pipe to the nitrogen cylinder.

- **Substrate inlet**

Reactor was provided with a single inlet for substrate and inoculum. The inlet was made singular as the cleaning of this inlet was quiet easy and the chances of it getting clogged were thin.

- **Gas outlets**

The reactor was provided with 2 gas outlets. This was to make sure that the second outlet could be used in case the first outlet is not operational. The functional outlet was connected via pipe to gas bag where the gas produced was being collected.

- **Reactor outlets**

Reactor was provided with 2 outlets as the outlets were directly in contact with the slurry inside and had every chance of getting clogged. The second outlet was made as a backup outlet in case the first outlet was clogged.

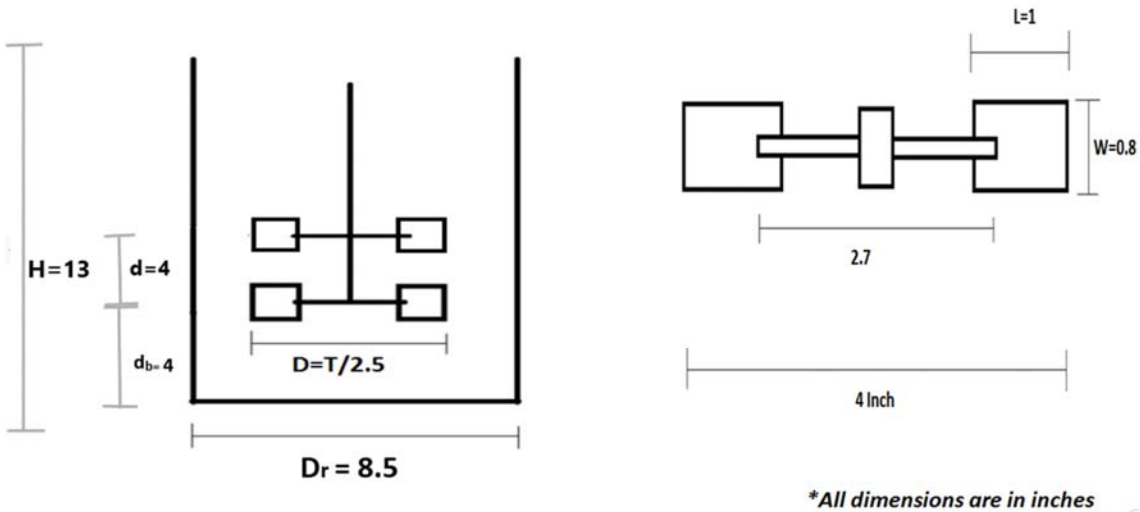


Figure 3.8 Reactor and Impeller Dimensions

3.7 Operating Conditions

The table 3.3 shows the operating conditions for biohydrogen production

Table 3-3 Operating Conditions for Dark Fermentation

Mode of Operation	Semi-Continuous
Scale	Semi-Pilot
Temperature	55°C
Inoculum-Substrate Ratio	0.1 on g VS basis
pH	5.5
Organic Loading Rate	25 ,33,50 g VS/L/d
HRT	24, 18 ,12 h

3.8 Operational Conditions of CSTR for Semi-Continuous Mode

The table 3.4 below shows the operational conditions for startup phase and operational phase of the CSTR.

Table 3-4 Operational Conditions of CSTR for Semi-Continuous Mode

Operational Runs of CSTR	Substrate	Duration	OLR	HRT
CS **Startup phase,** **Inoculum activation**	Corn starch	3 days	25gVS/L/d	24h
CS+FW **Startup phase** **Acclimatization period**	Corn starch + food waste	3 days	25gVS/L/d	24h
FW **Operational phase,** **Semi continuous mode**	Food waste	10 days	25gVS/L/d	24h
		10 days	33gVS/L/d	18h
		6 days	50gVS/L/d	12h

3.8.1 Start-up Phase

In reactor startup phase auxiliary substrate like cornstarch was used to activate the microorganism. After this mixture of equal weights of cornstarch and food waste was used to acclimatize the microorganisms to food waste.
The Hydraulic retention time was kept to be 24 hours while the Organic loading rate was 25 gVS/L/d and the duration was 3 days each.

3.8.2 Operational Phase

In the operational phase food waste was used alone. Operational phase had 3 Runs. Mass of food waste required to provide 250 g of VS was calculated and came out to be 1200 grams.
Since the inoculum to substrate ratio was 0.1 the amount of inoculum required was equal to 820 grams. These quantities were calculated on the basis of VS values of substrate and inoculum found as results of characterization.
The calculated quantities of both inoculum and substrate were added in 13 litre reactor and tap water was added in the digesters to completely cover the working volume i.e. 75% or

almost 10 L of the digesters leaving the remaining volume empty for the collection of biogas produced.

In Operational phase there were three Runs with organic loading rate of 25, 33, 50 (gVS/L/d) corresponding to HRT 24, 18, 12 (h). The duration for Run 1 and Run 2 was kept to be 10 days while the duration of Run 3 was 6 days

3.9 Gas Measurement and Collection

The gas produced inside the CSTR was collected in Devex Gas storage bags and measured by gas wet meter. Samples were taken in syringes

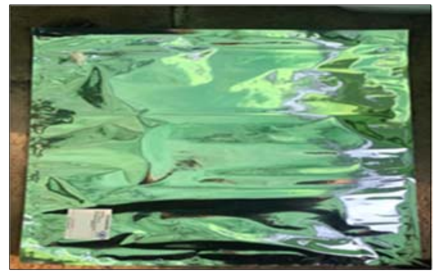


Figure 3.9 Devex Gas storage bags

3.10 GC Analysis

The gas produced from both the startup phase and operational phase was stored in Devex bags and syringes was sent for GC analysis to Centre for Advanced Studies in Energy NUST (CASEN) to determine the hydrogen percentage in the gas produced.

Figure 3.10 GC Apparatus

Chapter 4

RESULTS AND DISCUSSION

In this chapter we will be discussing characterization of Inoculum and Substrate used. Apart from this Effect of Varying Organic Loading Rate (OLR) on Volatile Fatty Acids (VFA) Production, Volatile Solids (VS) Removal, Hydrogen Percentage in biogas, Volumetric Hydrogen Production Rate (VHPR) and Hydrogen Yield (HY) for the three operational Runs will also be analyzed. In the end we have conclusions for the optimum Organic Loading Rate for which the volumetric hydrogen is maximum.

4.1 Substrate Characterization

4.1.1 Characterization of Components Used in Substrate

According to a comparative study in literature it was shown that the H_2 producing potential of carbohydrate-rich waste was approximately 20 times higher than that of fat-rich waste, therefore we performed physicochemical analysis on following carbohydrate rich potential substrates.

The Table 4.1 shows the result for individual characterization of each component used in the mixture. It can be seen that out of all the substrates lentils have the highest TKN value and boiled rice have lowest.

Table 4-1 Characterization of Components Used in Substrate

Characteristics	Tomato	Lentils	Boiled rice	Bread	Mixed vegetables
Moisture content	94.35	71.89	58.05	33.78	82.04
Total solids	5.65	18.11	41.95	66.22	17.96
Volatile solids	80.4	83.58	79.15	92.4	81.14
TOC (% of TS)	44.66	46.43	43.97	51.34	45.07
TKN (% of TS)	3.3	3.5	1.16	2.10	2
C/N	13.53	13.26	37.09	24.44	22.5

4.1.2 Substrate Percentage Composition on Weight basis

Based on our literature search, C/N Ratios of food waste should fall b/w 20 and 21 for optimum yield.

Keeping that in view the percentage composition, shown in the table 4.2, was so decided that the total C/N contribution of the components was equal to 20.

Table 4-2 Substrate Percentage Composition on Weight basis

Component	Percentage
Lentils	35
Bread	10
Boiled Rice	10
Mixed Vegetable	25
Tomato	20

4.1.3 Final Substrate Characterization

The decided percentage of each component was mixed to form a final substrate. Table 4.3 below shows the characterization of the final substrate.

Table 4-3 Final Substrate Characterization

Parameter	Unit	Results
Moisture Content	%	74
Total Solids	%	26
Volatile Solids	% of TS	79
Total organic carbon	% of TS	43.7
TKN	% of TS	2.2
C/N	---	20

4.2 Inoculum Characterization

Both of the digested cow dung and anaerobic sludge that were used as inoculums were tested for following parameters as shown in Table 4.4. Both were added to the reactor in a ratio of

1:1. It can be observed that TOC of Cow dung is more than anaerobic sludge because of the organic food intake of cows. Also the pH is less acidic this is because of the methanogens present in ruminants

Table 4-4 Inoculum Characterization

Component	Unit	Cow Dung	Anaerobic Sludge
Moisture Content	%	96	89
Total Solids	%	4	11
Volatile Solids	%TS	76.25	62
TOC	%TS	42.36	34
pH	--	6.8	5.43

4.3 Reactor Performance Indicators

Following reactor Performance Indicators were assessed each day

- VS Removal (%) was found out by simply measuring the VS content of the feed before loading and after the Hydraulic Retention time has passed.
- Total VFA(mg/L) is also a digester control test more important than pH was determined by titrating the effluent of the CSTR.
- Hydrogen % in biogas was simply measured through GC analysis from CAESN-NUST.
- Volumetric Hydrogen production rate (LH_2/Lreactor/d) was calculated by dividing the Litres of Hydrogen produced in one HRT dividing by reactor working volume and sampling time. Sampling time was equal to HRT as collection of gas was done after 1 HRT has passed.
- Hydrogen Yield (mmol/$gVS_{consumed}$) is a substrate utilization efficiency parmeter and is found about by dividing the milli moles of hydrogen produced divided by the $gVS_{consumed}$ (from VS removal).

4.3.1 Volatile Fatty Acids Production

The figure 4.1 shows the Effect of Varying Organic Loading Rate on Volatile Fatty Acids production for the three operational runs of CSTR.

The common trend observed was that VFA generation increased with increase in Organic loading rate. Initially at 25 the maximum VFA generation of 3004 mg/L was recorded followed by increment to 3599 mg/L (33) 4212 mg/L (50). Increase in VFA production also influenced pH and thus H_2 production. This increase in pH gradually reduces buffering capacity inside the CSTR.

The change in pH and Concentration of VFA is an indication of the metabolic processes involved in H_2 production

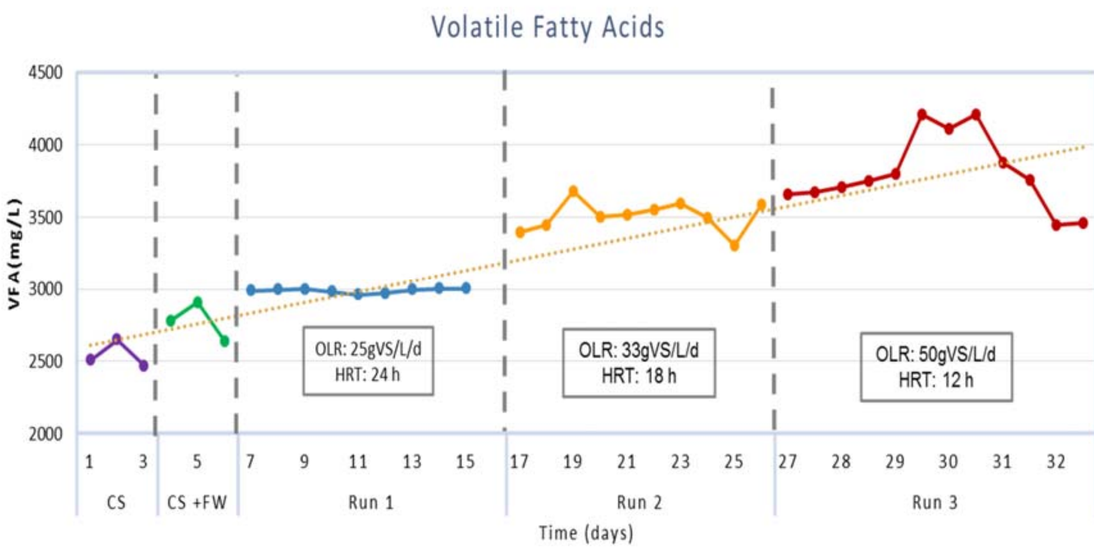


Figure 4.1 Effect of OLR on Volatile Fatty Acids

4.3.2 Gas production

The Gas produced was collected in Devex Bags for each Operational Run with different HRT and OLR and the volume produced was measured with gas wet meter.

From the figure 4.2 it can be observed that maximum gas production in terms of liters per day was observed for OLR-33 and HRT-18 of about 28L/d.

The minimum amount of gas was produced during the start-up phase because the Inoculum was not fully acclimatized to the system microenvironment at that time.

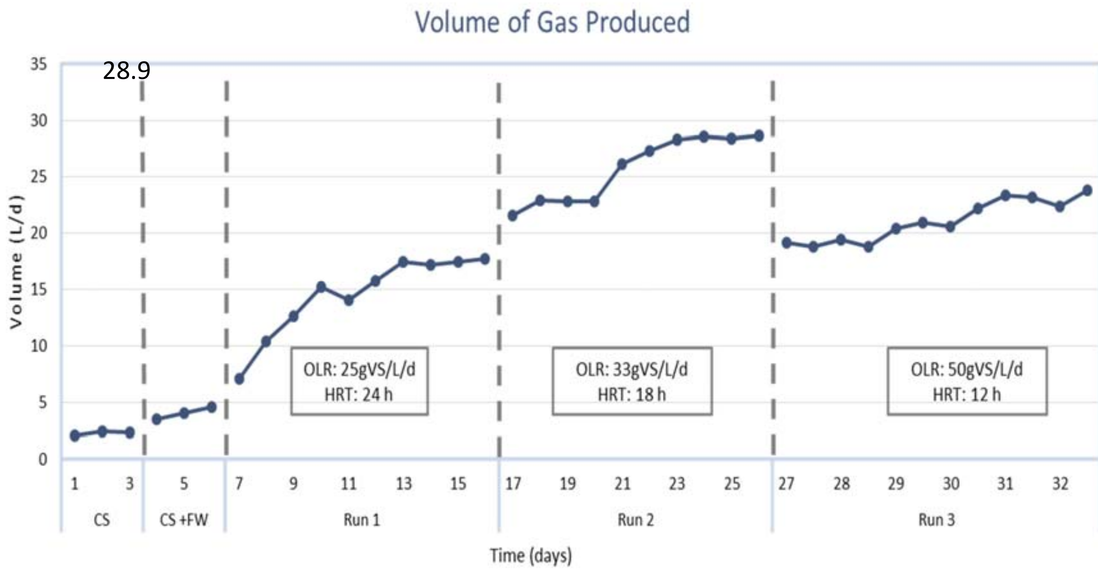


Figure 4.2 Effect of OLR on Volume of Gas produced

4.3.3 Hydrogen Percentage

Hydrogen percentages were obtained by conducting Gas Chromatography of the collected gas samples for both the start-up period and Operational Period. It can be seen from figure 4.3 that hydrogen gas produced during Run 3 corresponding to OLR-50 gVS/L/d has the highest percentage of hydrogen which is 39.7 while the lowest percentage is observed in startup phase when Corn starch was mixed with food waste. The results are also supported from literature, Hernandez et al. (2015) reported a H_2 percentage in biogas in a range from 25% to 55% for FW.

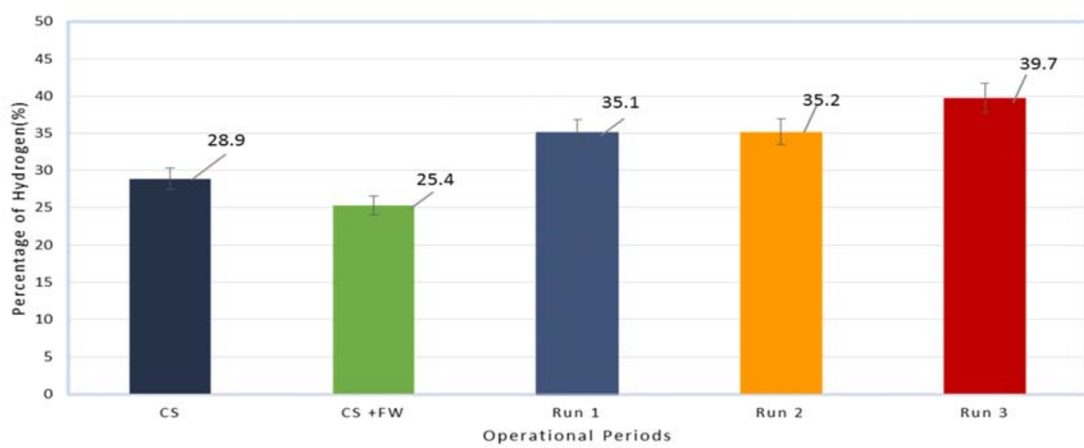


Figure 4.3 Hydrogen percentages at Different OLR

4.3.4 Gas Production versus Hydrogen Production

After calculating the percentages, hydrogen volume was calculated by multiplying the percentage of hydrogen with the total volume. The general trend observed was that Hydrogen Percentage increases with increasing OLR. The reason for this might be OLR-25 and OLR-33 has more amount of CO_2 and H_2S as compared to OLR-50.

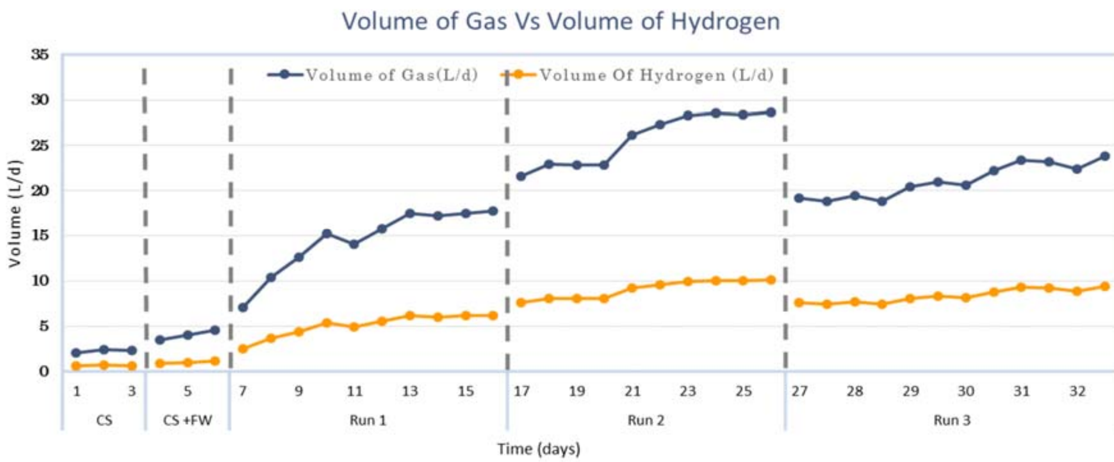


Figure 4.4 Comparison of Volume of Gas Vs Volume of Hydrogen per day

4.3.5 Volatile Solids Removal

Utilization of Food waste in the continuously stirred tank reactor for Hydrogen production was evaluated in terms of VS removal. From Figure 4.3 the general trend observed is that VS removal increases with increasing loading rate. VS removal was found maximum for Corn starch. However the shift from corn starch reduces the VS removal at first and increases afterwards. Out of the three OLRs for food waste alone maximum VS removal of 55.3 ± 0.4 was observed at 50gVS/L/d.

From the results it can be interpreted that increase in VS removal is because of the fact that increase on the waste load of food waste gradually acclimatize the system micro environment to Higher Organic loading rate.

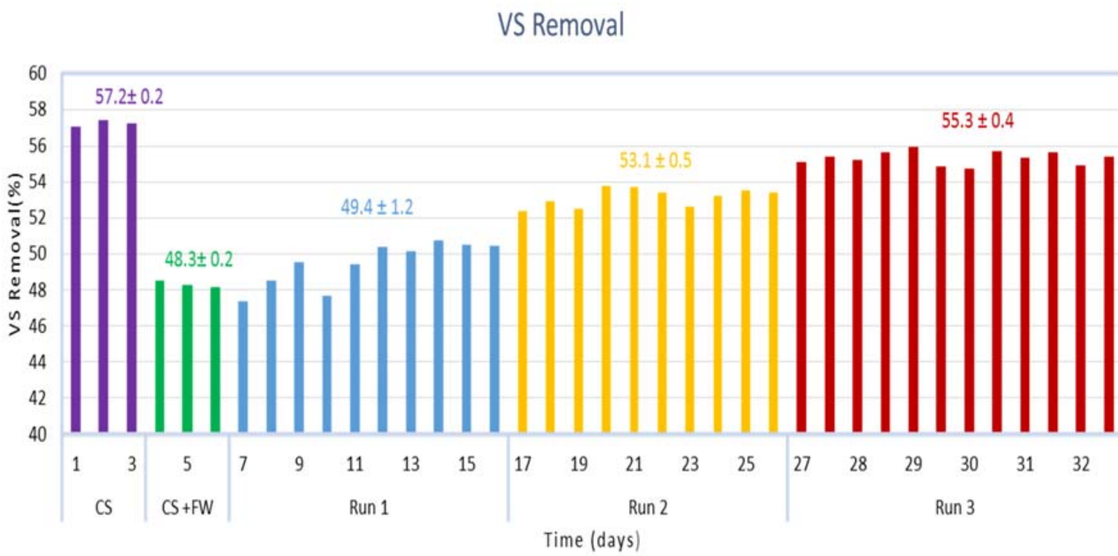


Figure 4.5 Effect of OLR on Volatile Solids Removal

4.3.6 Volumetric Hydrogen Production Rate

Figure 3.6 shows how organic loading rate influences on volumetric hydrogen production rate in the CSTR. It was observed that the highest VHPR of 1LH_2/L/d was achieved during the steady state at the end of the operational run for OLR 33gVS/L/d.

After conducting the T-test used for comparing the two data sets for statistical significance. For Run 1 and Run 2 the p value was less than the significance (0.05) indicating that the VHPR was statistically improved by the increase in OLR from 25gVS/L/d to 33 gVS/L/d. However for the data set of Run 2 and Run 3 the p value was a bit more than the significance value of 0.05, indicating that the decrease in VHPR by increasing OLR further is statistically insignificant.

The Increase in VHPR at first can be explained by increasing the amount of fresh substrate fed when the HRT was shortened, also at 50gVS/L/d fat might be the inhibition factor of anaerobic hydrogen production.

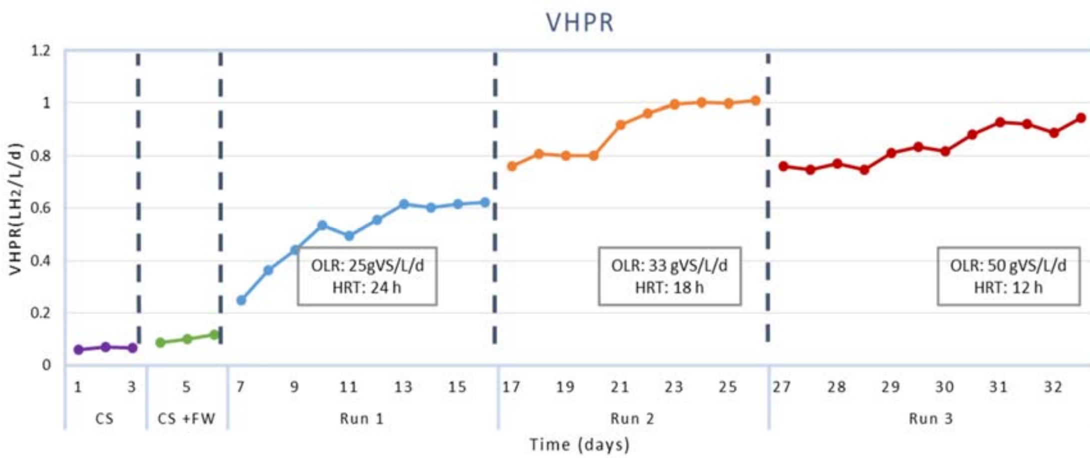


Figure 4.6 Effect of OLR on Volumetric Hydrogen Production Rate

4.3.7 Hydrogen Yield

Figure 4.7 represents the effect of OLR on Molar Hydrogen yield. The trend observed was that Hydrogen yield increases and is found maximum at 33gVS/L/d, reduces again at 50gVS/L/d. The decrease in H_2 yield at 50 leads us to the Interpretation that increase of the total VFA might affect the hydrogen yield.

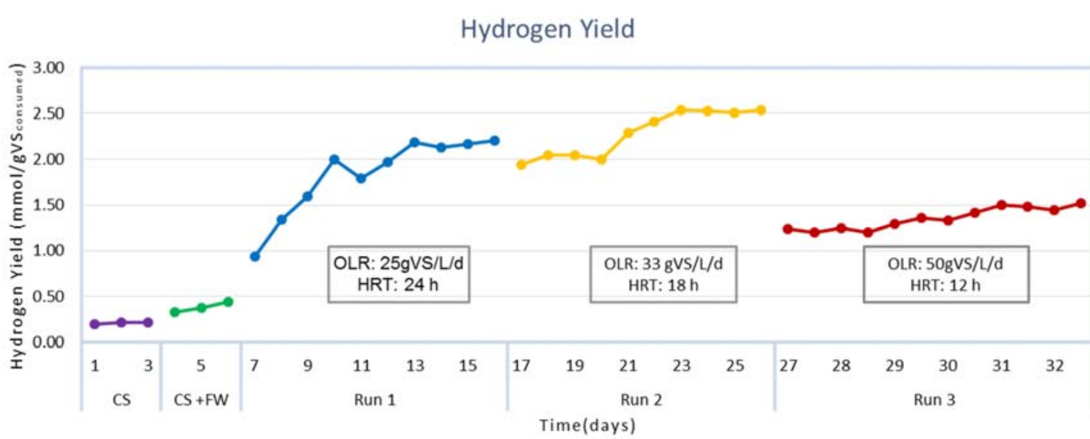


Figure 4.7 Effect of OLR on Molar Hydrogen Yield

4.3.8 Hydrogen Production Rate and Hydrogen Yield at different OLR

Figure 4.8 clearly shows that by comparing the Volumetric hydrogen production rate and Hydrogen yield at different OLR, maximum VHPR and maximum YH2 both occur at OLR 33

VS/L/d. This result is concordant with those obtained by Hafez et al where using glucose as a substrate, the maximum YH2 and VHPR were found at the same OLR.

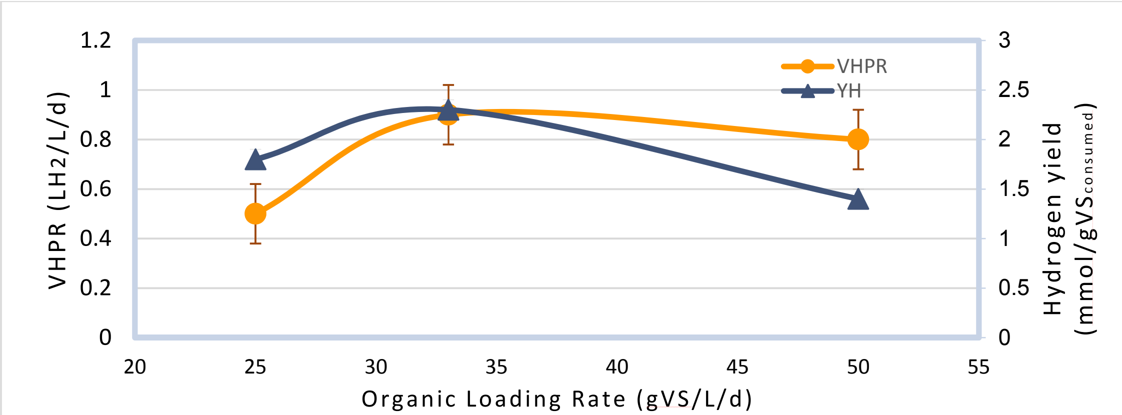


Figure 4.8 H_2 Production Rate and H_2 Yield at different OLR

Chapter 5

COST AND BENEFIT ANALYSIS

Decision to select a mechanical technology like CSTR for biohydrogen production from dark fermentation is always questioned as it is assumed to have high energy requirements. Its feasibility can only be justified by conducting a proper cost to benefit analysis.

5.1 Cost Discussion

Table… below shows the Capital Cost and Maintenance cost on yearly bases. The cost of stainless steel is 500/ft^2. From the dimension used for the reactor the surface area of the reactor was calculated. The surface area conforms to the land requirement.

Ringer et al. (2006) stated that the plants maintenance cost yearly will be 3% of the capital cost. Also the gas separation for obtaining pure hydrogen is 3% of the capital cost.

Table 5-1 Cost Estimation

Variables	Semi-pilot Scale	Cost (PKR)	Industrial Scale	Cost (PKR)
Capital Cost				
Stainless steel Reactor (Material + Manufacturing)	13 L	20,000	13000 L	2,000,000
Land requirement	5x5 square feet	23000	5 Marla	500,000
Motors required	1	2500	1 Motor	80,000
Pumps required	1	1500	Water and Gas pump + Screw bed pump	6,00,000
Yearly Operational and maintenance cost				
Operating Cost	Electricity + maintenance	3000	Running + maintenance	95400
Gas separation and Handling Cost	2 Gas bags	6000	Pressure Swing Adsorption	95400

Total Capital Cost at Industrial Scale = PKR 31,80,000

Operational and Maintenance Cost per year = PKR 1,90,800/yr

Total Investment for first year= PKR 33,70,800

5.2 Benefits Discussion

Table below represents the benefit obtained from the Project are in terms of

- Energy Efficiency
- Waste disposal
- Green house gas emissions

Table 5-2 Benefit analysis

Variables	Semi-pilot Scale	Cost Saving (PKR)	Industrial Scale	Cost Saving (PKR)
Money value of H2 (Rs/kg)	1415			
Kgs of H2 produced in 1 year	0.4	461.2	326	461138
Cost of Waste disposal (Rs/ton)	1355.2			
Waste Handled in 1 year (ton)	0.438 t	593.55	438	593577
Cost of 1 Carbon Credit (PKR/ton of CO2)	5094.9			
No. Of Certified emission reductions earned in 1 year	0.000682	3.47	3.27	16216

The money value of hydrogen is 1415 Rs/kg, and the total of 326 kgs of hydrogen will be produced per year indicating a cost saving of around 4 lakh 60 thousand.

Another benefit was in terms of waste handled per year, the waste handled per year on an industrial scale will be 438 ton and the cost of disposal per ton is Rs 1355 ,resulting in cost saving of about 5 lakh 93 thousand

The number of Certified Emission Reduction units earned in a year on an industrial scale were calculated by comparing the CO2 emissions from diesel with Hydrogen, the number of CERs earned will be around 3, and the cost of 1 carbon credit is around 5000, resulting in a cost saving of 16k

Total Benefit in 1 year at Industrial Scale = 461138.4 + 593577.6 + 16216.007

=PKR 1,070,932/ yr

Hence the total benefit of first year will be around 10 lakh 70 thousand

5.3 Payback Period

Total Capital Cost + O&M Cost = PKR 33, 70,800

Annual Cash Inflows =PKR 1,070,932

Payback Period = $\frac{Total\ Capital\ Cost + O\&M\ Cost}{Annual\ Cash\ inflows}$

Payback period = 3 years

On the basis of Cost Benefit the payback period of the project is around 3 years.

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Following conclusions were drawn from this study:

- The OLR has an influence on the H2 production in the CSTR, Volumetric hydrogen production rate increases with increasing OLR to a certain point and decreases afterwards on increasing OLR.
- The maximum Hydrogen yield (YH_2) Of 2.53 mmol/$gVS_{consumed}$ and highest VHPR of 1LH_2/L/d was obtained at an OLR of 33 gVS/Lreactor/d.
- VS removal of about 55…. was found maximum for OLR 55Gvs/L/d, this is because the system was well acclimatized to higher OLR and hence substrate utilization effiency was improved.
- Highest percentage of Hydrogen content of 39.. was also observed at OLR 55gVS/L/d.
- For a reactor to produce 10 LH_2/d, OLR 33gVS/Lreactor/d, requires least reactor size and hence cost effective.
- Since the maximal VHPR and YH_2 are obtained at OLR-33 while highest VS removal and Hydrogen percentage are observed at OLR-50, a compromise could be defined if both VHPR, YH_2 and VS removal, Hydrogen percentage, want to be maximized. However, since a low-cost substrate is used (OSW), it is possible to operate the reactor at the OLR which obtains the maximum VHPR.
- OLR of 33gVS/L/d is therefore recommended for an industrial scale system as it gave maximal HPR and YH_2

6.2 Recommendations

6.2.1 Recommendations for field application

In Pakistan hydrogen is largely produced from steam reforming of natural gas, which is both expensive and not environmental friendly therefore the produced H_2 produced, can be used in following industrial applications:

- Production of ammonia in Habers process
- Banaspati ghee Industries for Hydrogenation Reaction

- Energy Sector
- Automobile industries

6.2.2 Recommendations for future study

- It is highly recommended to test the potential of industrial effluents of industries like, Food industry waste, Textile industry, Sugarcane industry, Fruit and pulp industry because they contain high organic content.
- Conduct a study on a hybrid system that uses both Dark fermentation and Light Fermentation processes for better molar yields.

References

Agarry, Mujidat O. Aremu and Samuel E. (2012). “Comparison of biogas production from cow dung and pig dung under Mesophilic condition” International Refereed Journal of Engineering and Science, 1 (4), 16-21.

Chen, Chin-Chao, et al. (2012). "Thermophilic dark fermentation of untreated rice straw using mixed cultures for hydrogen production." International journal of hydrogen energy, 37 (20), 15540-15546.

Chong, Sabaratnam, Shiraic, Hassan (2009). "Biohydrogen production from biomass and industrial wastes by dark fermentation." International journal of hydrogen energy, 34(8), 3277-3287.

Ciro F., Pirozzi D., Ausiello A., Micoli L., Pasquale V., Toscano G., Turco M., Dumontet S. (2017). “Effect of Inoculum/Substrate Ratio on Dark Fermentation for Biohydrogen Production from Organic Fraction of Municipal Solid Waste.” Chemical Engineering Transactions, 57, 175-180.

Duangmanee, Thitimaporn & I Padmasiri, S & J Simmons, J & Raskin, Lutgarde & Sung, Shihwu. (2007). “Hydrogen Production by Anaerobic Microbial Communities Exposed to Repeated Heat Treatments.” Water Environment Federation, 79 (9), 975-983

Gustavsson, Cederberg, Sonesson (2011). “Global Food Losses and Food Waste: Extent, Causes and Prevention.” Food and Agriculture Organization of the United Nations.

Han W., Yan Y., Shi Y., Gu J., Tang J. & Zhao H. (2016). “Biohydrogen production from enzymatic hydrolysis of food waste in batch and continuous systems.” Nature Scientific Reports, 6, 383-395.

Jacqueline Xiao Wen Hay, Ta Yeong Wu, Joon Ching Juan, Jamaliah Md. Jahim. (2013). “Biohydrogen production through photo fermentation or dark fermentation using waste as a substrate: Overview, economics, and future prospects of hydrogen usage. Biofuels, Bioprod. Bioref, 7(3) 334–352

Jarunglumlert, Teeraya & Prommuak, Chattip & Putmai, Namtip & Pavasant, Prasert (2017). "Scaling-up bio-hydrogen production from food waste: Feasibilities and challenges." International Journal of Hydrogen Energy, 43(2), 634-648.

Khanal (2011). "Anaerobic biotechnology for bioenergy production: principles and applications." John Wiley & Sons.

Kongjan, O-Thong, Kotay, Min, Angelidaki (2010). "Biohydrogen production from wheat straw hydrolysate by dark fermentation using extreme thermophilic mixed culture." Biotechnology and bioengineering, 05 (5) 899-908.

Kumar, Gopalakrishnan & Shobana, Sutha & Nagarajan, Dillirani & Lee, Duu-Jong & Lee, Kuo-Shing & Lin, Chiu-Yue & Chen, Chun-Yen & Chang, Jo-Shu. (2018). "Biomass based hydrogen production by dark fermentation-recent trends and opportunities for greener processes." Current opinion in biotechnology, 50, 136-145.

Lee, Ze-Kun & Li, Shiue-Lin & Lin, Jian-Sheng & Wang, Yu-Hsuan & Kuo, Pei-Chen & Cheng, Sheng-Shung. (2008). "Effect of pH in fermentation of vegetable kitchen wastes on hydrogen production under a thermophilic condition." International Journal of Hydrogen Energy, 33 (19,) 5234-5241.

Monroy, Isaac, Péter Bakonyi, and Germán Buitrón (2018). "Temporary feeding shocks increase the productivity in a continuous biohydrogen-producing reactor." Clean Technologies and Environmental Policy, 20 (7), 1581–1588.

Vazqueza, Navarroa, Colunga, Rodríguezb, Flores. (2009). "Continuous biohydrogen production using cheese whey: improving the hydrogen production rate." International Journal of Hydrogen Energy, 34 (10) 4296-4304

Venegas, Morales, Illanes, Fernando & Toledo, Javiera & Paillet, Florian & Escudie, Renaud & Lay, Chyi-How & Chu, Chen & Leu, Hoang-Jyh & Marone, Antonella & Lin, Chiu-Yue & Kim, Dong-Hoon & Trably, Eric & Ruiz-Filippi, Gonzalo. (2015). Biohydrogen production by dark fermentation: scaling-up and technologies integration for a sustainable system. Reviews in Environmental Science and Bio/Technology, 14 (4), 761–785.

Waligorska (2012). "Fermentative Hydrogen Production – Process Design and Bioreactors" Chemical and Process Engineering, 33(4), 585-594.

Yasin, Nazlina Haiza Mohd, Tabassum Mumtaz, and Mohd Ali Hassan (2013). "Food waste and food processing waste for biohydrogen production: a review." Journal of environmental management, 130 (C), 375-385.

Yun, Lee, Im, Marone, Trably, Shin, Cho, Kim (2018). "Biohydrogen production from food waste: Current status, limitations, and future perspectives." Bioresource Technology, 248 (A), 79-87.