Addis Ababa Institute of Technology

School of Mechanical and Industrial Engineering

Simulation, Experimental Analysis of Biogas Upgrading and Compressing of Produced Biomethane For A 10m^3 Biogas Plant: Case Study at Sidistkilo Campus

A Thesis Submitted to The School of Graduate Studies of Addis Ababa University in Partial Fulfillment of The Requirement for The Degree of Master of Science in Thermal Engineering

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CANDIDATES DECLARATION

I hereby declare that the work which is being presented in the thesis entitled "Simulation and Experimental Analysis of Biogas Upgrading and Compressing of Produced Biomethane For A 10m^3 Biogas Plant" in partial fulfillment of the requirements for the award of the degree of Master of Science in thermal Engineering is an authentic record of my own work carried out from February 2017 to June 2018 under the supervision of Dr.ing Wondwossen Bogale Department of Mechanical and industrial engineering , Addis Ababa institute of technology Ethiopia. The matter embodied in this thesis has not been submitted by me for the award of any other degree or diploma. All relevant resources of information used in this thesis have been duly acknowledged.

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge. This thesis has been submitted for examination with my approval.

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ABSTRACT

Upgrading and compressing of natural gas provides a safer and cheaper alternative energy source for transportation, electrical production and also increases its storage capabilities. The global use of natural gas is growing quickly. This is primary attributed to its favorable characteristics and to the environmental advantages it enjoys over other fossil fuels such as petroleum, oil and coal.one of the key challenges in supplying natural gas is the form (phase) at which it should be delivered. Natural gas like biogas maybe supplied to the consumer by upgrading to reduce contaminates and finally as a compressed gas or through pipe lines. when there is a considerable distance involved in transporting natural gas.

The present study focuses on development of a gas cleaning and compressing step for a product gas produced in a biogas plant. Removal of contaminants from biogas can therefore significantly improve the gas quality. The study shows that the Theoretical potential of waste and residues for biogas production is around 230kg/day of caferia food wasted which is produced about 9.987m^3/day biogas and 3.74 kwh/day using the energy conversion method from a biogas plant. This work addresses the simulation and experimental investigation of biogas Upgrading and compression from biomethane production of 10m^3 biogas plant of food waste. The purification study was investigated using combined chemical methods of (activated carbon, NaOH, KOH, Wood charcoal and silica gel) improving the calorific value of biogas. Experiment results revealed that the chemical solution used effectively in reacting with CO_2, H_2S, H_2O in biogas (over 80–96%) removal efficiency, creating CH_4 enriched biogas. The experimental result shows these innovative technologies reduce the acidic content H_2S by 96 % and removes the CO_2 by 80-90 %. Thus, the Methane content has been increased from 56.7 % to 87 %. The CO_2 content reduces from 36 % to 10 %. First the process flow sheet is constructed based on the common process configuration. Then the key parameters taken from literature are simulated using MATLAB 2017 to determine amount of chemical needed for each g of gas produced in streams of the plant.

Keywords: Biogas, upgrading, compressing, activated carbon, silica gel, NaOH, electricity generation

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ABBREVIATIONS

AD = anaerobic digestion

MSW = municipal solid waste

TS = total solid

VS = volatile solid

CW = caferia waste

VW = vegetable waste

Fw = fruit waste

VOC = volatile oxygen content

CBG = compressed biogas

CNG = compressed natural gas

VSA = vacuum swing adsorption

PSA = pressure swing adsorption

R = compression ratio

v_{gas} = volume of gas in the tank

$v_{tr,N}$ = volume of dry gas in normal state

$C_{CH_4,tr}$ =methane volume fraction in the dry gas

$C_{CH_4,f}$ = methane volume fraction in the moist gas

NPV = net present value

BCR = benefit cost ratio

SPP = simple payback period, I_c = initial cost

CHAPTER ONE

1. Introduction

1.1. Background history

The requirement of energy across all major segments of the world depends on fossil fuels and responsible for the fast depletion of resources in order to improve lifestyle and because of the fast population growth there must be a search for renewable source of energy so that one of the renewable sources is biomethane which is produced as a result of production of biogas.

Biogas is produced when organic material is decomposed under anaerobic condition in a digester chamber. It is the mixture of methane and carbon dioxide produced by the bacterial decomposition of sewage, manure, garbage, or plant crops [1]. Raw biogas consists mainly of methane (CH_4, 40-75%) and carbon dioxide (CO_2, 15-60%). Trace amounts of other components such as water (H_2O, 5-10%), hydrogen sulfide (H_2S, 0.005-2%), siloxanes (0-0.02%), halogenated hydrocarbons (VOC, < 0.6%), ammonia (NH_3, <1%), oxygen (O_2, 0-1%), carbon monoxide (CO, <0.6%) and nitrogen (N2, 0-2%) can be present and might be inconvenient when not removed. its higher heating value is between 15 and 30MJ Nm-3 [2].

Table 1.1 composition of biogas (Source: Bori et al. 2007)

Component	Composition
CH_4	40-75%
CO_2	15-45%
H_2S	0.001-2%
H_2	0.01-2%
N_2	0.1-4%
O_2	0.02-6.5%
Ar	0.001%
H_2O	3-10%
CO	0.001-2%
NH_3	Trace

One of the most important components of municipal solid waste is Food waste, it including household food waste, food-processing waste, and cafeteria and restaurant waste. The estimated amount of FW sharply increased from 2.78 billion tons to 4.16 billion tons in Asian countries by 2025 [4] for the production of biogas as a renewable energy demand to meet the requirement of energy needs of the community and reducing biomass energy source like wood, dung, charcoal for the reduction of deforestation, soil erosion (degrading of soils) and for the healthy use of energy in the society.

The highly increasing Energy consumption demand of the world is because of the account of developing technology, industrialization and increasing population. In the recent times fossil fuels are the significant amount of world primary energy demand and reserve of these resources decrease rapidly [1].especially in the developing countries, produced energy doesn't meet the consumed energy, and dependence on foreign sources is getting increased and on the other hand combustion of fossil fuels and utilization of oil based transportation fuels increases amount of carbon dioxide (CO_2) and other greenhouse gases emission in the atmosphere(Perego and Ricci 2012).finally fossil fuels have a regeneration cycle time less than their usage ratio, which makes them non-renewable resource. For all of those reasons we have to determine a rational policy that requires the use of new and renewable Owen energy resource and eco-friendly fuel and material technology.

For the sustainable production of green chemicals and biofuels biomass is the most plenty economic, easy accessible ,clean with net zero CO_2 emission and sustainable renewable source with an important potential.it is a good alternative to solve the problem of fossil fuel and their products by processing (upgrading and cleaning) biogas to biomethane (Demirbas 2009a,Zhou et al 2011).at the present in the international market, first generation biofuels biodiesel and bioethanol dominates as the most widely today for transportation among the first-generation biofuels (Taylor 2008).bioethanol is mainly derived from plants plenty in carbohydrates and starch and it is a substitute of petroleum gasoline.in contrast, biodiesel is a substitute of petroleum diesel and it's produced from vegetable oils and animal fats (Demirbas 2011).

Upgrading and compressing is the most promising technology among the thermochemical routes to convert biomass to compressed biomethane valuable products via complex chemicals and physical reaction. Bio oils, bio-crudes or polyols obtained via liquefaction of biomass can be upgraded to gasoline and diesel like fuels and various polymeric materials. The range of application of biogas technology with which we are working is currently being limited to applications in the developing world such as India, Africa, and the Philippines for uses such as cooking fuel and heating homes [3, 4].

A significant majority of these products could be obtained from cleaned/upgraded biomass particularly biomass-based wastes in the near future. For this reasons biomass upgrading and compressing has a great potential. The aim of this study is Development of cost effective technologies available for upgrading and compressing biogas using some commonly used conventional upgrading technologies connected with a small-scale compressing and bottling plant to produce compressed bio-methane for purpose of substituting diesel as a transportation fuel, considering the petroleum export cost increment and minimizing environmental impact of using diesel fuel. CO_2 also used for coca cola bottling companies.

The physical and chemical properties of biogas are not suitable for injection into the natural gas grid or for utilization with actual end use converters therefore purification of trace compounds and CO_2 including moisture. the promising rout for the production of biomehtane is the utilization of biogas purification and upgrading. And this is performed not only to enable its usage in wider applications but also to increase its heating value, calorific value and relative density of the biogas by the removal of non-combustible CO_2 and to prevent corrosion of different components like compressors, gas storage tanks, pipes and engines. For this all above concerns the upgrading process must be performed to maximize the purity and energy capacity of biogas including the concern of environmental benefits.

Cleaning of biogas is needed because of two main reasons;

- To improve the calorific value of the product gas
- To reduce the chance of damaging downstream equipment which is due to the Formation of harmful compounds (Ryckebosch et al., 2011)

The use of biogas as a clean energy resource answers to current concerns dealing with economics, ecology and energetics:

- Search on renewable energies while the fossil deposits are draining,
- Reduction of the energetic dependence,
- Limitation of the atmospheric pollution linked to the gas emissions,
- Decrease of the smell and noise annoyances
- Reduction of the green house effects.
- Economical efficient use of fuels
- Replacing standard diesel fuel to minimize environmental hazard and cost

This paper aims to upgrading and compressing biomethane produced from food waste for some specific purposes like using in a gas grid injecting as transportation fuel and minimizing energy dependence on petroleum's, burning biomass products. This process was under going through

- A cleaning process, in which the trace components harmful to the natural gas grid, appliances or end-users are removed
- CO_2 is removed to adjust the calorific value and relative density in order to meet the specifications of the Wobble Index.

1.2. Biochemical Process of Anaerobic Digestion

Anaerobic digestion is a process of controlled decomposition of biodegradable materials under managed conditions where free oxygen is absent, at temperatures suitable for naturally occurring mesophilic or thermophilic anaerobic and facultative bacteria and archaea species, that convert the inputs to biogas and whole digestate. It consists in the biochemical degradation of complex organic matter resulting in the biogas production, which has as main constituents' methane (CH_4) and carbon dioxide (CO_2), and trace amounts of hydrogen (H_2), nitrogen (N_2), ammonia (NH_3) and hydrogen sulfide (H_2S). The significant number of biodegradable components (carbohydrates, lipids and proteins) present in the microalgae biomass makes it a favorable substrate for the anaerobic microbial flora that can be converted into biogas rich in CH_4. The process occurs in the stomachs of animals, and the same biological process found in nature can be replicated and controlled by engineers. There are four major steps of anaerobic digestion, shown in figure 1.

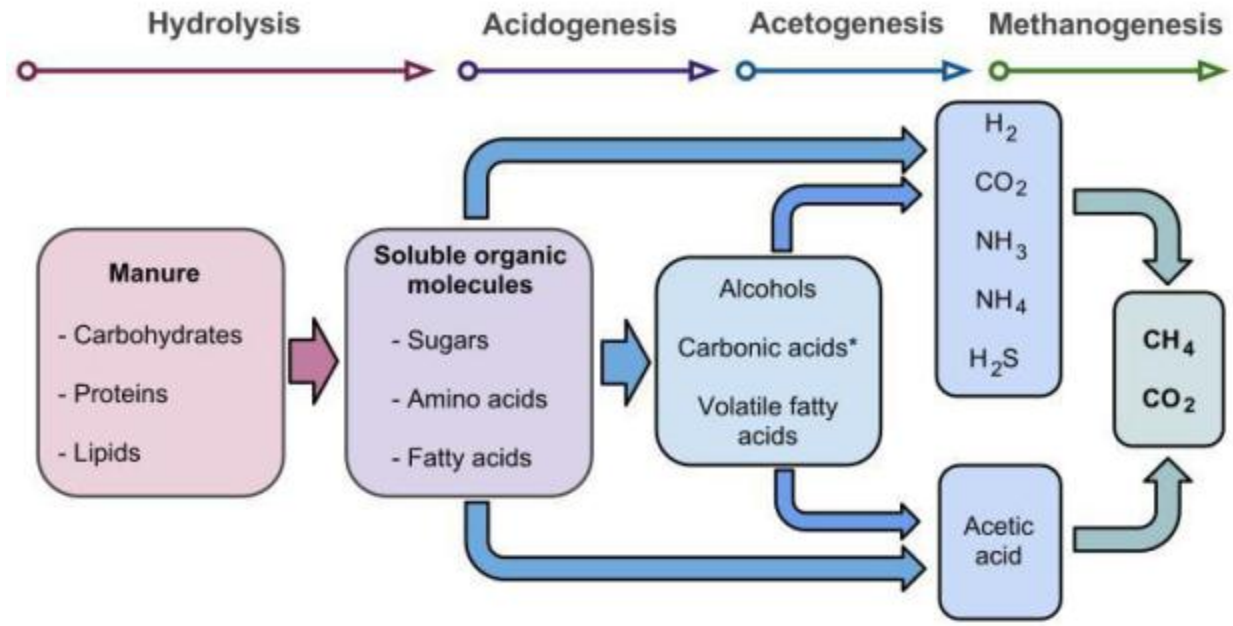


Figure 1.1 The anaerobic digestion pathway

1.3. General properties of biogas

Table 1.2 General properties of biogas (Deublein & Steinhauser, 2011)

Methane content	55-77% (CH4)
Energy content	6-6.5 KWh/m^3
Fuel equivalent	0.60-0.615oil m^{-3} biogas
Explosion limit	6-12% biogas in air
Critical pressure	75-89 bar
Ignition temperature	650-750^{o}C
Critical temperature	-82.5°C
Normal density	1.2 kg m^{-3}
smell	Bad eggs

1.4. Problem statement

Due to the challenges of limited fossil-fuel resources and stringent emission norms, interest in developing clean and sustainable energy sources has grown considerably. Biofuels, derived from biomass and thus being renewable, biodegradable and oxygenated, are receiving increasing public and scientific attention. The concept of upgrading biogas and compressing finally bottling using a recommended technology for the purpose of transportation fuel and other electrical energy was not a new concept rather it is developed through a long time ago for centuries. But the most important source of energy in Ethiopia is wood biomass; cow dung and mainly the diesel fuel in our machineries are other non-Environmental friendly sources. This hassled to soil degradation, deforestation, global warming, and air pollution and associated diseases due to indoor air pollution.

Since all biogas streams commonly contain harmful impurities, such as CO_2, H_2S, water (moisture) and siloxanes which shorten the life of kitchen stove parts that include burners, pressure regulators and gas meters. The presence of H_2S in the biogas contributes to formation of highly corrosive acid that attacks metal parts upon combustion and interaction with water vapor. This result to corrosion and fouling of burners and lowers the calorific value (CV) of the gas as well. The high presence of CO_2 in the biogas not only hinders its compressibility into gas cylinders but also is the main reason for low CV as it does not support combustion. In view of underlying problems, it is necessary to remove the contaminants to improve the quality of the gas.

Due to the rapid depletion and high cost of liquid fuel, natural gas is used in a compressed form named compressed biogas (CBG). Currently, it has become very popular alternative to liquid fuel for vehicles in the world due to its low price. the upgrading and compressing processes of biogas is a continuum research from the case study done in sidist kilo campuses i.e. producing biogas from cafeteria food waste for electric generation since the case study describes there is a 230 kg waste of food only from the first cafeteria producing of about 20litter of biogas. From two cafeterias the result will be doubled and so that the main intention of this paper is upgrading, compressing and bottling from the biogas obtained because of the rising cost of imported petroleum and transport fuel products, with the rising highly consumption demand of fuels and biomass energy scarcity, there is a need of up graded biogas to meet the requirement of the customer and for the purpose of green environment.

1.5. Objectives

1.5.1. General objective

Through our research we aim to design and develop experimentally examined biogas purification and compressing system which is very economical, as well as, environment friendly to achieve this we must compare and contrast different upgrading and compression systems, in order to find the most cost-effective small-scale (proto type) demonstrative plant by Developing a process simulation models of chemicals for biogas upgrading or gas cleaning system to simultaneous removal of CO_2 and H_2S and producing a gas enriched with CH_4 (87%).

1.5.2. Specific objective

- Describe how biogas is upgraded and selecting the main components in a biogas compressing system
- Magmatically modeling, simulation and experimental demonstration of the cleaning system to get the minimum amount of chemicals used in the process.
- Developing a process flow sheet model of operations used in the treatment of food waste and upgrading of biogas.
- Based on the integrated model predicting the maximum amount of methane purity that can be produced from food waste after the removal of CO_2, H_2S and H_2O
- Analyze the biogas composition before and after upgrading
- Economic analysis of the upgrading plant

1.6. Scope and significance of the study

This research study of small scale biogas up grading, compressing and bottling is basically deals on the purification and cleaning of impurities available in biogas in an efficient and economical way through out an experimental investigation in a laboratory scale.so that our basic intention is by purifying methane through applying our small scale experimental analysis we can develop to an industrial scale with some specific and basic upgrading equipment’s for some specific purposes, like electrification, heating, cooking and for gas grid injection etc. so that this research can serve as a foundation for future research on scaling up of similar works. The outcome of the study will help for energy and environmental protection policy makers as a reference.

During preparation of a guideline for increasing number of alternative renewable energy technology means by using different resources, for substitution of fossil fuel throughout the country and for managing the city food substrate wastes. In general, it contributes to the economic advancement of the country through production of energy from food wastes which reduce the amount of fuel import from abroad and it has great impact on reduction of greenhouse emission from livestock industry substituting upgraded biogas as a basic energy source

1.7. Motivation

- Reduce energy consumption and reduction of Emission of greenhouse gases
- Presence of CO_2 reduces the heating value of the gas and may cause problems with gas combustion equipment.
- Presence of water reduces the heating value of gas. It may also form gas hydrates and cause corrosion.
- H_2S is a poisonous gas and is highly corrosive. In order to reduce the wear on process equipment and piping, and for safety reasons, it should be removed as early as possible.
- CO_2 is a potent greenhouse gas and should be removed and stored to prevent it from entering the atmosphere.

CHAPTER-TWO

2.1. Literature review

The beginning of managing waste products has developed before a long period of time and also the improvement, technological advancement ways of waste treatment methods are highly and constantly increased. The process of anaerobic reaction for the production of biogas in one of the most crucial waste treating advanced methods for minimizing organic waste products and highly accumulated sludge’s. During the process of anaerobic digestion, breaking down of the complex organic materials to a single substances results with a high production of biogas. biogas can be burned for direct heating, or it can be used in a combined heat and power plant to generate power and electricity. Another interesting, developed and ongoing option is upgrading of biogas into biomethane, can serve and substitute a fuel the transportation sectors.

The degree of microbial decomposition of food waste for producing biogas used as substrate mainly depends upon its chemical composition. It is quite challenging to know the exact percentage of different components of the complex substrate because of its heterogeneous nature. Various researchers have been investigating the potential of food waste as a substrate for biogas production and biomethanation.

Biogas Upgrading and bottling is a renewable energy source which can help both in waste management and in building a clean and sustainable environment. This technology is an economically viable option for biogas produced at medium to large scales. Biogas generated from anaerobic digestion process is a clean and environmentally friendly renewable fuel. However, it is important to clean and upgrade before using it to increase the CV and making it usable in some gas appliances (Mathieu, 2009)

Due to Its increased usage of biogas in many ways, such as production of heat and steam, electricity production and co-generation, vehicle fuel, feedstock for the production of bio-based chemicals and substrates in fuel cells, starting reactants in chemical processes, substitute for natural gas for domestic and industrial use, and gas grid injections. Biogas production shows an increased trend in recent years. So, Biogas purification and upgrading had been researched extensively in recent years. ***Xiu and Shahbazi*** [5] summarized the state of the art technology for producing and upgrading bio-oil, with the focus on the hydrothermal liquefaction process.

Abatzoglou and Boivin [1] reviewed biogas purification with the focus on the removal of contaminants, such as H_2S, NH_3, and siloxanes, but the removal of CO_2 was only briefly mentioned. ***Weiland*** [6] presented an overview of the complete biogas production and consumption chain but did not focus on currently available upgrading technologies

Bekkering et al. [7] studied the current status and future options of biogas upgrading technologies but did not present the technical performance and economic report on various upgrading technologies. ***Ryckebosch et al***. [2] reviewed different biogas upgrading technologies with the focus on their operating conditions, drawbacks, and efficiency. ***Pertl et al***. [8] and ***Starr et al***. [9] applied life cycle assessment (LCA) to biogas upgrading ***Bauer et al***. [10] found that the market shares for biogas upgrading technologies have been changed rapidly in recent years, amine scrubbing is continuously achieving significant market shares, and a competition between pressure swing adsorption (PSA) and high-pressure water scrubbing (HPWS). ***Kárászová et al***. [11] reviewed membrane separation processes for biogas and found that membrane gas permeation is able to compete with classical biogas upgrading technologies. However, researchers still need to solve the challenges in using membrane for the removal of volatile organic compounds (VOC) and siloxanes from raw biogas. ***Sun et al***. [12] encouraged more researches on membrane separation (upgrading) process for economical biogas upgrading and its utilization as a vehicular fuel as it is more beneficial for the environment. ***Chen et al***. [13] revealed that hybrid processes for biogas upgrading are more efficient, where membrane separation is combined with absorption, adsorption, and cryogenic technique. This combined separation processes can improve the performance and reduce the operational cost of the process.

Compressing the biogas reduces the storage requirements, concentrates energy content and increases pressure to the level required overcoming resistance to gas flow. Compression is better in the scrubbed biogas. Biogas produced from poultry manure is being dried, scrubbed, compressed and stored at a pressure of 4 bars in 0.2 m^3 steel tanks in Belgium [14]. ***Khapre*** [15] conducted a study on scrubbing and compression of biogas and subsequently used it for domestic cooking. He found reduced requirement of scrubbed and compressed biogas (0.353 m^3) than raw biogas (0.591 m^3) for cooking a day’s meal of a six-member family. He stored the scrubbed and compressed biogas at a pressure of 7 bars in cylinder of 0.1 m^{3}capacity. ***Nema and Bhuchner*** [16] stressed on value addition to biogas by scrubbing and compressing, making it as good as the compressed natural gas (CNG). They reported the economic feasibility of producing energy from solid wastes of Delhi city. From 5000 tons' wastes are generated per day in Delhi, 100,000 Nm^3/day biogas can be produced which is equivalent to 309.5 m^3 CNG worth US $ 70,000 per day. By purifying the biogas produced from the distillery wastes, scientists of ***Jadhavpur University, Kolkatta, India*** [17] claimed to have generated huge quantities of compressed methane, a gas with an immense potential and an alternative source of vehicle fuel. ***Yang et al***. [18]. Reviewed the research progresses and industrial applications on converting biogas into biomethane. ***Sharifzadeh et al***. [19] emphasized the importance for upgrading bio-oil from biomass fast pyrolysis in order to achieve the synergy between CO_2 utilization and biomass production

The capital and operating costs of biogas upgrading technologies largely depend on the selected process, quality of raw biogas, desired product quality, and more importantly, the capacity of the plant, the specific investment cost of various upgrading technologies significantly depends on the plant capacities; the smaller the capacity (0–100 Nm^3/h) the higher the specific investment cost and vice versa. For a plant with low capacity, more or less the same number of equipment, sensors, control valves, and pipes are required as for a plant with much larger capacity. The dimensions of the pipes and valves will be small, but the investment cost will be high.

The recent market for matured biogas upgrading technologies highly depends on its optimization design with low operational cost. from the above existing reviews and studies, we have explored the concepts and comprehensive investigation of purification system, the techno-economic performance of biogas upgrading technologies, their developments, energy requirements, market shares, and environmental analysis, utilization of upgraded biogas, and conversion and storage of bio-CNG. So, from the summery of the above literatures of different types of upgrading studies is summarized and investigated. But in this paper, we are adopted a chemical absorption applying (Activated Carbon, Silica Gel and Sodium Hydroxide) an upgrading technology based on technology based on its energy requirement, maintenance cost, technical availability per year, complexity of process, in expensiveness of raw materials and achievement of a CH_4 purity of 80–85%.

2.2. Biogas Quality and Standards

Biogas can be used for all applications designed for natural gas, assuming sufficient purification. Greer (2010) has shown that biogas quality and energy content are critical to many applications generating heat. A biogas conditioning and upgrading system typically integrates several technologies to meet equipment or process specifications for end use applications. Selecting the right technologies for application depends on gas composition, project scale, economics and operational consideration.

Table 2.1 Biogas Utilization Technologies and Gas Processing Requirements (Chaudhary, 2004)

Technology	Recommended gas processing unit
Heating(boilers)	H_2S <1000ppm,0.8-2.5kpa pressure, remove condensate (Kitchen stoves:H_2S <10ppm
Internal combustion engine	H_2S <1000ppm,0.8-2.5kpa pressure, remove condensate and siloxanes (Otto cycle engines more susceptible to H_2S than diesel engines)
Micro turbines	H_2S tolerant to 70,000 ppm,>350 BTU/scf, 520 kPa pressure, remove condensate, remove siloxanes
Sterling Engines	Similar to boilers for H_2S, 1-14 kPa pressure
Natural Gas Upgrade	H_2S < 4 ppm, CH4 > 95%, CO2 < 2% volume, H_2O < (1 x 10^{-4}) Kg/MMscf, remove siloxanes and particulates, > 3000 kPa pressure

2.3. Biogas Energy Potential and its Natural Gas Equivalent

It can be seen that CH4 is the main component for both gases being at 91% in natural gas and 55– 70% for biogas. Further, CO_2 and H_2S content are much higher in biogas as compared to the natural gas and this is the main difference between the two gases. The Wobbe Index which is defined as the CV per specific gravity of gas is the best indicator of the similarity between natural gas and biogas. It characterizes the gas in a manner that is useful for blending fuel gases, or to obtain a constant heat flow from a gas with variable composition. It can be seen that the wobbe index for natural gas is about twice that of the biogas.

In order to blend fuel gas or obtain a constant calorific value from a gas having variable composition the wobbe index have to be made similar. Consequently; only gases with a similar Wobbe index can substitute each (Zhou et al., 2011).

Table 2.2 Physical Properties of Natural Gas and Biogas (Zhou et al., 2011)

Key numbers	**unit**	**Natural gas**	**biogas**
Methane (CH_4)	Vol%	91	55-70
CO_2 (carbon dioxide)	Vol%	0.61	30-40
N_2(nitrogen)	Vol%	0.32	0-2
H_2S (hydrogen sulfide)	Ppm	~1	100-50,000
Net calorific value	MJ/m^3	39.2	23.3
Upper wobbe index	MJ/m^3	54.8	27.3
Lower Wobbe index	MJ/m^3	49.6	25.1
Adiabatic flame temperature	^{o}C	2040	1911

Table 2.3 Pure component properties (Thermodynamics Research Center, 2014)

Component	**Methane (CH_4)**	**Unit**
Molecular weigh	16.043	g mol^{-1}
Normal boiling point	111.6539	K
Critical volume	0.09928	m^3 kmol^{-1}
Critical pressure	4599949.2	N m^{-2}
Critical temperature	190.5631	K

2.4. Cleaning and upgrading of Biogas

Biogas cleaning is the first necessary step in biomethane production. Although this paper is focused on biogas upgrading (cleaning) and compressing technologies, it is necessary first to have an overview of existing cleaning technologies that always will act as a pretreatment in the whole process to prevent corrosion and mechanical wear of the upgrading equipment itself. Several commercial techniques for biogas upgrading exist today and, on the other hand, new techniques are continuously under development.

In order to improve the quality of biogas from an aerobic digestion it must pass two major processes: -

- A cleaning process, in which trace components harmful to the appliances or end-users are removed.
- An upgrading process, in which the CV (calorific value), Wobble index and other parameters are improved in order to meet the natural gas equivalence

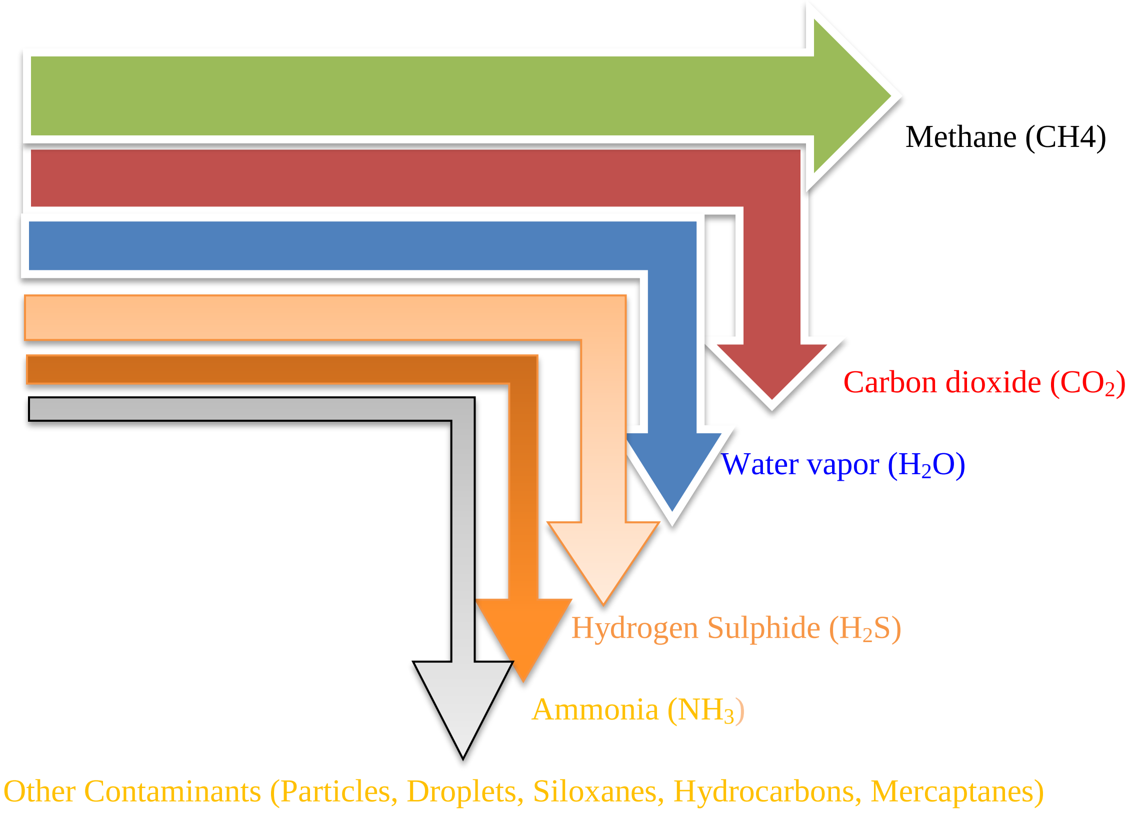


Fig 2.1 sequence of impurities that must be cleaned from biogas

Table 2.4 Content and effect of typical impurities (Deublein & Steinhauser, 2011)

Component	**content**	**Effect**
CO_2	25-50 Vol %	• Lowers the calorific value • Increases the methane number and the anti-knock properties of engines • Causes corrosion (low concentrated carbon acid), if the gas is wet • Damages alkali fuel cells
H_2S	0-0.5 Vol %	• Corrosive effect in equipment and piping systems (stress corrosion); many manufactures of engines therefore set an upper limit of 0.05 volume % • SO_2 emissions after burners or H_2S emissions with imperfect combustion – upper limit 0.1 volume %

		and Spoils catalysts
NH_3	0-0.05 Vol%	• NO_x emissions after burners damage fuel cells • Increases the anti-knock properties of engines
Water vapour	1-5 Vol %	• Causes corrosion of equipment and piping systems • Condensates damage instruments and plants • Risk of freezing of piping systems and nozzles
dust	>5μm	• Blocks nozzles and fuel cells
dust	0-5 Vol %	• Lowers the calorific value • Increases the anti-knock properties of engines
siloxanes	0-50mg m^{-3}	• Act like an abrasive and damages engine

2.4.1. Removal of Water

Biogas always contains water vapors that have to be removed to avoid corrosion in pipelines and equipment's. Water can be eliminated by physical separation (cooling and compression) and chemical drying (absorption and adsorption). Refrigeration or cooling preceded or not by compression, is the simplest way of removing excess water vapor. The condensed water can be then separated using demisters, cyclones or water traps [2]. Adsorption using alumina, silica gel or zeolites is the most common technique [20]. Also, hygroscopic salts or triethylene glycol can be used.

a) Techniques Using Physical Separation of Condensed Water Include:

- Demisters in which liquid particles are separated with a wired mesh (micropores 0.5-2 nm). A dew point of 2-20 ^oC (atmospheric pressure) can be reached;
- Cyclone separators in which water droplets are separated using centrifugal forces;
- Moisture traps in which the condensation takes place by expansion, causing a low temperature that condenses the water;
- Water taps in the biogas pipe from which condensed water can be removed [22]

b) Methods Based on Chemical Drying Method (Absorption or Adsorption)

2.4.1.1. Adsorption of water vapor on silica, alumina or equal chemical components that can bind water molecules (adsorption dryer): - Usually two columns are used in parallel: one column adsorbs water, while the other is being regenerated. Regeneration is achieved by evaporating the water through decompression and heating.

- A part of the dried gas is led through the column and recycled to the compressor inlet. Silica, activated carbon, aluminum oxide or magnesium oxide can be used for the drying process. Using adsorption dryers, a dew point from -10 to -20 ^oC (atmospheric pressure) can be achieved [21,22].

***2.4.1.2. Absorption of water in triethylene glycol*: -** (Drying takes place by using the water binding component triethylene glycol. Used glycol is pumped into a regeneration unit, where a temperature of 200 ^oC is used to regenerate the glycol. Dew points from -5 to -15^oC (atmospheric pressure) can be reached [22].

2.4.1.3. Absorption of water with hygroscopic salts: - The salt is dissolved as it absorbs water from the biogas. The saturated salt solution is withdrawn from the bottom of the vessel. The salt is not regenerated and new salt granules have to be added to replace the dissolved salt [21]

2.4.2. Removal of H_2S

H_2S concentration in the biogas can be reduced by preventing its migration to biogas during digestion process or by treating the gas stream [21, 23]. In the first case, the addition of iron ions to the digester precipitates the iron sulfide that will leave the rector with the digestate. In the second case, adsorption on activated carbon, iron oxide or hydroxide [24], washing with ***sodium hydroxide*** or biological treatment [25] are all well-known options.H_2S can be also separated from the biogas by leading the gas by a semi-permeable membrane [26].

2.4.2.1.Air/oxygen dosing to the biogas system

This technique is based on the biological aerobic oxidation of H_2S to elemental sulfur by a group of specialized microorganisms. Most of those sulfides oxidizing micro-organisms (Thiobacillus) are autotrophic and use CO_2 from the biogas to cover their carbon need. They grow on the surface of the digestate or on the framework of the digester and do not require inoculation. The following reaction occurs in the biogas:

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \qquad (2.1)$$

Not only elemental sulfur, but also sulfate is formed, which can cause corrosion in solutions. A small amount (2-6%) of O_2 needed for the reaction to occur is introduced in the biogas System by an air pump. A reduction of H_2S concentrations down to 20-100 cm^3 and a removal efficiency of 80-99% can be achieved [27, 28]. However, the remaining concentrations may still be too large to enable use of the biogas as a substitute for natural gas [22]. Safety measures have to be taken to avoid overdosing of air: biogas in air (6-12%) is an explosive mixture. Care has to be taken that anaerobic conditions remain present in order to keep the digestion process from being inhibited.

2.4.2.2.Addition of iron chloride into the digester

Iron chloride can be dosed directly into the digester or through the influent mixing tank. It reacts with the H_2S present in the biogas to form FeS (particles). The precipitation reaction of the iron salt can be written as follows: -

$2Fe^{3+} + 3S^{2-} \rightarrow 2FeS + S$ …………………………………………………………… (2.2)

$Fe^{2+} + S^{2-} \rightarrow FeS$ ……………………………………………………………................ (2.3)

Due to the precipitation of FeS, the presence of H_2S in the biogas is avoided. This method is very efficient in reducing high concentrations of H_2S, but less efficient in achieving a low and stable level of hydrogen sulfide necessary for vehicle fuel quality or pipeline quality biomethane [28].

2.4.2.3.Adsorption using iron oxide or hydroxide

Hydrogen sulfide reacts easily with iron oxide, iron hydroxide and zinc oxide and forms iron sulfide or zinc sulfide respectively. This process is often referred to as “iron sponge” because rust-covered steel wool may be used to form the reaction bed. Steel wool, however, has a relatively small surface area, which results in low binding capacity for the sulfide. For this reason, wood chips impregnated with iron oxide have been used as preferred reaction bed material since they have a larger surface-to-volume ratio. Iron oxide or hydroxide can also be bound to the surface of pellets made from red mud, a waste product of the Bayer process gaining aluminum out of Bauxite. With these pellets an even larger surface-to-volume ratio can be reached [28].

Iron oxide, iron hydroxide and sodium hydroxide react with H_2S in the biogas according to following reactions: -

$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O$ ………………………………………………………… (2.4)

$2Fe\,(OH)_3+3H_2S\rightarrow Fe_2S_3+6H_2O$………………………………………………………….......... (2.5)

$Na\,(OH)_2 + H_2S\rightarrow NaS+2H_2O$………………………………………………………………. (2.6)

The reaction is slightly endothermic: a temperature minimum of about 12°C is required to provide the necessary energy. The reaction is optimal between 25 and 50°C.Condensation of water on the iron oxide should be avoided since the iron oxide material will stick together with water which reduces the reactive surface [27]. The iron oxide can be regenerated with oxygen according to the following reaction: -

$2Fe_2S_3+3O_2\rightarrow 2Fe_2O_3+6S$……………………………………………………………….. (2.7)

This reaction is exothermic and therefore a large quantity of heat is released during regeneration. This may lead to self-ignition of the wood chips, if air flow and temperature are not carefully controlled. Typically, two reaction beds are installed. One bed undergoing regeneration while the other bed is removing H_2S from the biogas [28]. The former elementary sulfur remains on the surface and blocks the active iron oxide or hydroxide, restricting the number of cycles that can be performed [27].

2.4.2.4.Absorption with liquids

Absorption of H_2S in liquids can be either physical or chemical. Physical absorption involves dissolving the trace component in the solvent, whereas chemical absorption involves dissolving the component followed by a chemical reaction of the trace component and the solvent. Physical absorption removes H_2S by absorption in water or an organic solvent [22]. The most common solvent is water scrubbing being a robust technique although operational disturbances due to the growth of micro-organisms on the packing occur. Two types of water absorption processes are commonly used for the upgrading of biogas: single pass absorption and regenerative absorption [29]. A high consumption of water is needed if there is no regeneration step involved. Adding chemicals in water can improve the absorption process, resulting in lower water and energy consumption due to reduced pumping. Chemical absorption liquids that can be used are:

- Diluted NaOH-solution: NaOH reacts with H_2S to form Na_2S or NaHS which precipitates. The formed sodium salts are not regenerative and have to be disposed of

- $FeCl_2$-solution: This process is based on the formation of insoluble FeS that needs to be removed
- Fe (OH) $_3$-solution: H_2S is removed using Fe (OH) $_3$ resulting in the formation of Fe_2S_3. Regeneration is done with oxygen or air (closed system) [22]. Horikawaet al. (2004) [30] investigated chemical absorption of H_2S in a Fe (III) catalyst solution. In this process, H_2S is dissolved in an aqueous solution and catalytically removed by a chelated iron according to the following reaction.

$S^{2-} + 2Fe^{3+} \leftrightarrow S + 2Fe^{2+}$ ……………………………………………………………………. (2.8)

The sulfur produced is easily separated by sedimentation or filtration from the Fe-solution. Regeneration of the aqueous Fe-solution is done by oxygenation, followed by conversion of the pseudo-catalyst into its active form Fe^{3+}

$1/2O_{2\,(aqu)} + 2Fe^{2+} \leftrightarrow 2Fe^{3+} + 2OH^-$……………………………………………….…………(2.9)

Due to the regeneration the Fe-solution can be retained entirely and a large consumption of chemicals is avoided. The process can be carried out at ambient temperature and is very specific in removing H_2S: the volumes of the other biogas components CH_4 and CO_2 remain nearly constant. Moreover, a removal of 90 -100% can be obtained for biogas containing 2.2% H_2S at a gas flow of 1 $dm^3\ min^{-1}$, the catalytic solution flowing at 83.6 $cm^3\ min^{-1}$ and an inlet biogas pressure of 220 kPa [30]. At lower catalytic solution flow, lower absorption efficiency is obtained. At lower inlet H_2S concentration higher absorption efficiency is obtained. Therefore, the total removal of H_2S depends on the use of the adequate ratio of gas to liquid flow rates [30].

2.4.2.5.Adsorption on activated carbon

H_2S can also be removed by using activated carbon, which is often dosed with KI or sulfuric acid (H_2SO_4) to increase the reaction rate. In biological filters the H_2S is catalytically converted to elemental sulfur and water.

$2H_2S+O_2 \leftrightarrow 2S+2H_2O$……………………………………………………………………... (2.10)

Before entering the carbon bed 4e6% air is added to the biogas. The former elementary sulfur is adsorbed by the activated carbon. Best efficiency is obtained at pressures of 700-800 kPa and temperatures of 50-70^{o}C. This temperature is easily achieved through heat generation during compression. If a continuous process is required the system can consist of two vessels [21, 27, and 31]. One vessel for adsorption and the other for regeneration. Regeneration can be performed with hot nitrogen (inert gas) or steam. The sulfur is vaporized and, after cooling, liquefied at approximately 130^{o}C. Typically, the activated carbon is replaced rather than regenerated [24, 34, 32].

Table 2.5 Alternatives for H_2S removal from gas streams (Freira, 2000; Ryckebosch et al, 2011)

	Alternatives	Reactions	Range of application	Advantage	Disadvantage
regeneration	Redox	$2Fe^{3+}+H_2S \rightarrow 2Fe^{2+}+S+2H^+$	0.5-0.15tons/day of H_2S	Elemental S is formed high removal efficiency use of low toxicity solutions	Requires specialized super vision, low quality product, high pressure problems
	Amines	$RNH_2+H_2S \rightarrow (RNH_3) + 2S$ $RNH_2+H_2S \rightarrow RNH3 + HS$	H_2S concentration higher than 30 ppm and gas flows higher than 10000m3/day	High removal efficiency for H_2S and CO_2	cost
	Ferric oxide	$2Fe(OH)+3H_2S \rightarrow Fe_2S_3+6H2O$ $Fe(OH)_2+H2S \rightarrow FeS+2H_2O$ $2Fe_2S_3+3O2+6H2O \rightarrow 4Fe(OH)_3+3S_2$ $2FeS+O_2+2H_2O \rightarrow 2Fe(OH)+S_2$	Low scale	Most used. High removal efficiency (>99%)	Inappropriate for medium scale application reagent disposal
	Activated carbon	adsorption	Low scale	Elemental S is	Absorbs

					formed	methane
non-regeneration	Solid reagents	Zinc oxide	$ZnO+H_2S \rightarrow ZnS+H_2O$		Low cost High selectivity Operational Flexibility Low CO_2	Disposal of saturated reagent
		Iron oxide	$Fe_2O_3+H_2S \rightarrow 2FeS+S+3H_2O$ $Fe_3O_4+H2S \rightarrow 3FeS+S+4H_2O$			
		Sodium nitrite	$3H_2S+NaNO_2 \rightarrow NH_3+3S+NaOH+XNOx$ $2NaOH+H_2S \rightarrow Na_2S+2H_2O$			
	solvent	Caustic washes	$CaO+H_2O \rightarrow Ca(OH)_2$ $Ca(OH) +H_2O \rightarrow Ca(CO)3 +H_2O$ $CaO +H_2S \rightarrow CaS +H_2O$	0-300ppm H_2S concentration	Elemental S is formed low cost low removal efficiency for H_2S and CO_2	Operational difficulties Disposal of saturated solution
		Permanganate solutions	$3H_2S +2KMnO_4 \rightarrow 2H_2O+2MnO_2+2KOH$			
		water	adsorption			
biological			Uses bacteria or microorganisms under controlled ambient conditions	50-20000kg/day of H_2S	Elemental S is formed	Incomplete H_2S absorption needs extra treatment. Required strict control of bacterial condition
			Adsorption with filter		High removal possible >97% Low operational cost	

2.4.3. Removal of Siloxanes

The removal of siloxanes is mainly necessary for landfill gas and biogas originated by digestion of municipal waste since its origin is in cosmetics, pharmaceuticals and anti-foam products. Siloxanes can be removed by cryogenic separation (cooling), adsorption on activated carbon, silica gel or activated aluminum [33] and physical absorption in liquid mixtures of organic solvents [34], strong base or strong acid. The removal of siloxanes is mainly necessary for landfill gas and biogas originating from municipal waste, because they are present in significant concentrations (1-400 mg m^{-3}). Schweigkofler and Niessner (2001) [20] investigated the efficiency of different liquid and solid materials in the removal of siloxanes. Siloxanes can be removed by physical absorption with long carbon chain organic solvents in a spraying device or a packed column. Thermal regeneration of silica gel and activated charcoal is performed at 250^{o}C for about 20bar. Silica gel gives excellent regeneration of more than 95% while similar studies using activated coal were less effective. Humidity plays an important role in the removal of siloxanes with silica gel: more humidity decreases the efficiency. There for a dehumidification step must be performed before siloxanes are removed. Silica gel beds can be operated at elevated pressure, achieving simultaneously a very effective biogas drying and a quantitative siloxanes removal. Experiments with silica gel show that its removal capacity is larger than with activated carbon. At large scale, silica gel could be a better and economically more interesting adsorbent to remove siloxanes, but more research is needed to subscribe this.

2.4.4. Removal of oxygen / air

Oxygen and nitrogen can be present in the biogas if air has intruded the digester or the gas collector (quite often in landfills). Oxygen and nitrogen removal is expensive because membranes, activated carbon, pressure swing adsorption or catalytic oxidation [35] should be use. Air introduction prevention by careful monitoring is the best option [2].

2.4.5. Removal of Ammonia

Ammonia is present in the biogas when the original substrate is rich in nitrogen. It could be removed from the biogas by a washing process with diluted acid or with activated carbon, but it is usually separated when the biogas is upgraded, without a separate cleaning step.

2.4.6. Removal of CO_2

Upgrading biogas to natural gas quality is a multiple step procedure. After removal of water (vapor), H_2S, siloxanes, carbon hydrates and NH_3, the removal of CO_2 is necessary in Order to obtain the quality that meets the Wobble Index [31]. Depending on its intended use (pipeline or vehicle fuel), biomethane consists typically of 97- 99% methane and 1-3% CO_2. Typical pipeline specifications require a CO_2content of less than 3% whereas vehicle fuel specifications require a combined CO_2N_2 content of 1.5 - 4.5% [32]. One of the following techniques can be used to remove CO_2 from the biogas:

(1) Physical and chemical CO2-absorption,

(2) Pressure Swing Adsorption (PSA) and Vacuum Swing Adsorption (VSA),

(3) Membrane separation,

(4) Cryogenic separation and

(5) Biological methane enrichment

Table 2.6 Techniques for removal of CO_2 (Ryckebosch et al, 2011)

method	advantage	disadvantage
Absorption with water	High efficiency (>97% CH_4) Simultaneous removal of H_2S when H2S<300cm^{3}m^{-3}, easy in operation Capacity is adjustable by changing pressure or temperature Regeneration possible Low CH4losses (<2%) Tolerant for impurities	Expensive investment Expensive operation Clogging due to bacterial growth Foaming possible Low flexibility toward variation of input gas
Absorption with polyethylene glycol	High efficiency (>97% CH4) Simultaneous removal of organic S components,	Expensive investment Expensive operation Difficult in operation Incomplete

	H_2S, NH_3, HCN and H_2O Energetic more favorable than water Regenerative Low CH_4 losses	regeneration when stripping/vacuum (boiling required) Reduced operation when dilution of glycol with water
Chemical absorption with amines	High efficiency (>99% CH4) Cheap operation Regenerative More CO_2 dissolved per unit of volume (compared to water) Very low CH_4 losses (<0.1%)	Expensive investment Heat required for regeneration Corrosion Decomposition and poisoning of the amines by O_2 or other chemicals Precipitation of salts Foaming possible
PSA/VSA Carbon molecular sieves Molecular sieves (zeolites) Alumina silicates	Highly efficient (95e98% CH4) H_2S is removed Low energy use: high pressure, but regenerative Compact technique Also, for small capacities Tolerant to impurities	Expensive investment Expensive operation Extensive process control needed CH_4 losses when malfunctioning of valves
Membrane technology Gas/gas Gas/liquid	H_2S and H_2O are removed Simple construction Simple operation High reliability Small gas flows treated without proportional	Low membrane selectivity: compromise between purity of CH_4 and amount of upgraded biogas Multiple steps required (modular system) to reach high purity CH_4 losses

	increase of costs Gas/gas Removal efficiency: <92% CH_4(1 step) or>96% CH_4 H_2O is removed Gas/liquid Removal efficiency: - >96% CH4 Cheap investment and operation Pure CO_2can be obtained	Little operational experience
Cryogenic separation	90-98% CH_4 can be reached CO_2 and CH_4 in high purity Low extra energy cost to reach liquid biomethane (LBM)	Expensive investment and operation CO_2 can remain in the CH_4
Biological removal	Removal of H_2S and CO_2 Enrichment of CH_4 No unwanted end products	Addition of H_2 Experimental not at large scale

2.5. Biogas upgrading and purification technologies

The technical features of various upgrading technologies are currently developed and the most available upgrading systems on industrial scale include the following: -

2.5.1. Pressure swing adsorption (PSA)

Pressure Swing Adsorption (PSA) is a process based on the mechanism that gas molecules can be selectively adsorbed to solid surfaces according to molecular size. The PSA technology can be used to separate CH_4 from N_2, O_2 and CO_2, since the CH_4 molecule is larger than the other gas molecules. The adsorption material used for biogas upgrading adsorbs H_2 S irreversibly, and thus H_2 S is considered toxic to PSA [36]. For this reason, initial removal of H_2 S is required prior to PSA. The concentration of CH_4 after upgrading is typically about 96–98% and CH_4 losses are about 2–4%. However, 10–12% methane losses were observed in an investigation of two PSA plants, although the equipment supplier claimed that the losses should be below 2% [37]. In general, more CH_4 is lost at higher purity requirements Due to the high concentration of CH_4; the vent gas has to be properly treated before being released into the atmosphere, for example by being burnt in a flox burner.

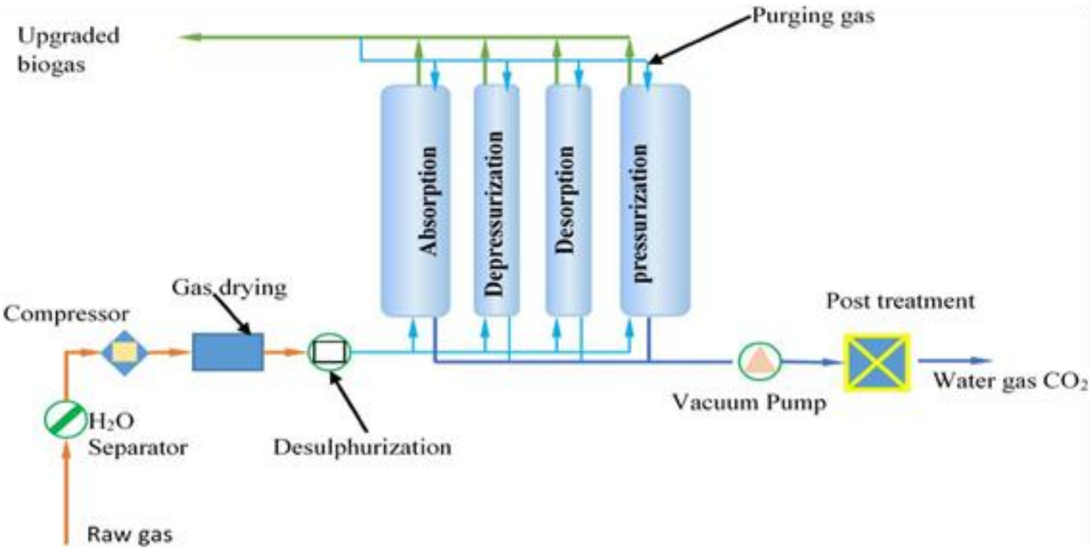


Fig 2.2 process flow diagram of pressure swing absorption

2.5.2. Water scrubbing

Water is used as a solvent in water scrubbing. The solubility of CH_4 in water is much lower than that of CO_2. In principle, H_2S can be removed together with CO_2, since the solubility of H_2S in water is higher than that of CO_2. However, because gaseous H_2S is poisonous and dissolved H_2S can cause corrosion problems, pre-separation of H_2S is normally necessary. Water scrubbing can achieve a CH_4 purity of 80–99%, depending on the volume of non-condensable gases such as N_2 and O_2 that cannot be separated fromCH_4. The CO_2 released from water regeneration is usually not collected. Except with air stripping, it is possible to achieve high purity of CO_2, up to 80–90%. The CH_4 losses, mainly due to dissolution in water, are usually between 3% and 5% according to theoretical calculations, although equipment suppliers sometimes claim that the losses can be controlled to below 2% [38]. The energy consumption in water scrubbing is mainly used for compressing raw gas and processing water by circulation pumps. In the processes involving air stripping, the air fan for water regeneration also consumes a small amount of electricity**.**

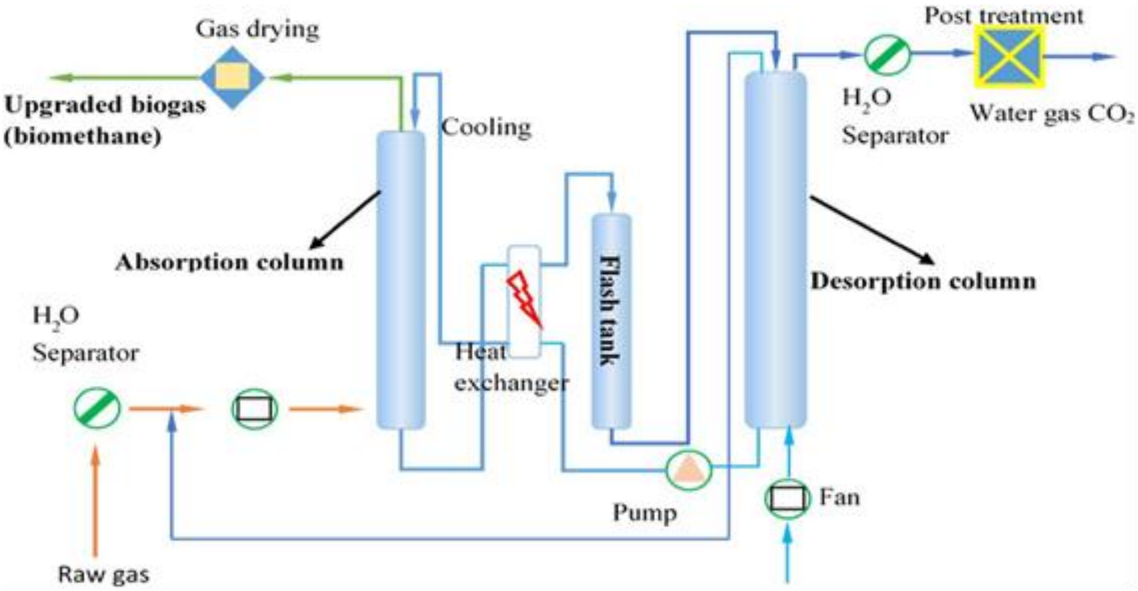


Fig 2.3 process flow diagram of pressurized water scrubbing system

2.5.3. Cryogenic separation

Due to the different condensing temperatures of CH_4 and CO_2, CO_2 can be separated from CH_4 through condensation and distillation. The technology for cryogenic separation is still underdevelopment, but some commercial plants are already in operation [39]. To avoid freezing and other problems in the cryogenic process, water and H_2S need to be pre-separated out. When CH_4 is condensed, N_2 and O_2can also be separated out. Since the cryogenic separation process needs to compress raw gas to a high pressure, e.g. up to 200 bar, a large amount of energy, accounting for 5–10% of the bio methane produced, is needed in the process [37]. Cryogenic separation shows great advantages in producing liquid and high-purity bio methane and the losses of CH_4 can be very low, usually lower than 1%. In addition, high purity CO_2, up to 98% purity, can also be produced from cryogenic separation.

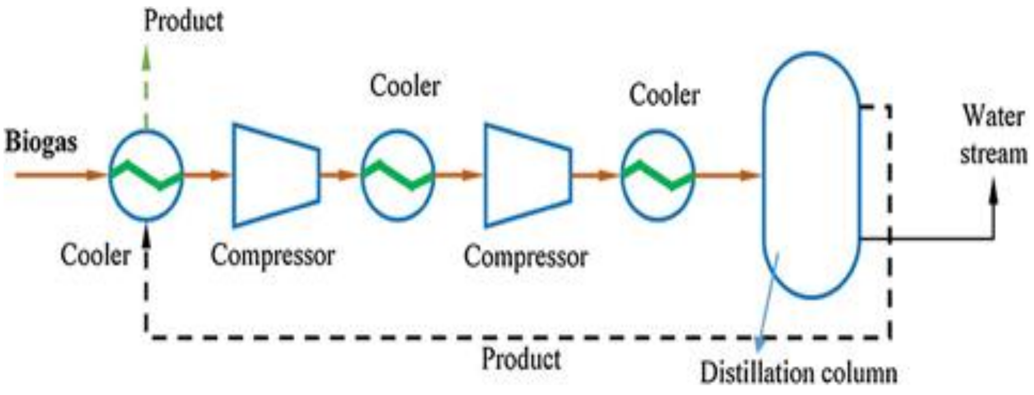


Fig 2.4 process flow diagram of Cryogenic separation

2.5.4. Physical absorption

The principle of physical absorption is the same as that in water scrubbing. Instead of water, organic solvents such as methanol and dimethyl ethers of polyethylene glycol (DMPEG) can be used to absorb CO_2 [40]. Therefore, physical absorption also has similar characteristics to water scrubbing, such as the inability to remove N_2 and O_2 and high losses of CH_4. However, since CO_2 has a higher solubility in organic solvents, the upgrading system can be more compact and part of pumping work can be avoided. It is also necessary to separate out H_2S prior to the absorption process, because it is difficult to regenerate H_2S from the solvent and this will reduce the capacity for CO_2 absorption. This process can produce CO_2 of high purity, but unfortunately there is no available information on this in the literature. The energy consumption of Physical absorption is comparable to that of water scrubbing. In addition to electricity, heat at a temperature of 55–80℃ is needed to regenerate the solvent.

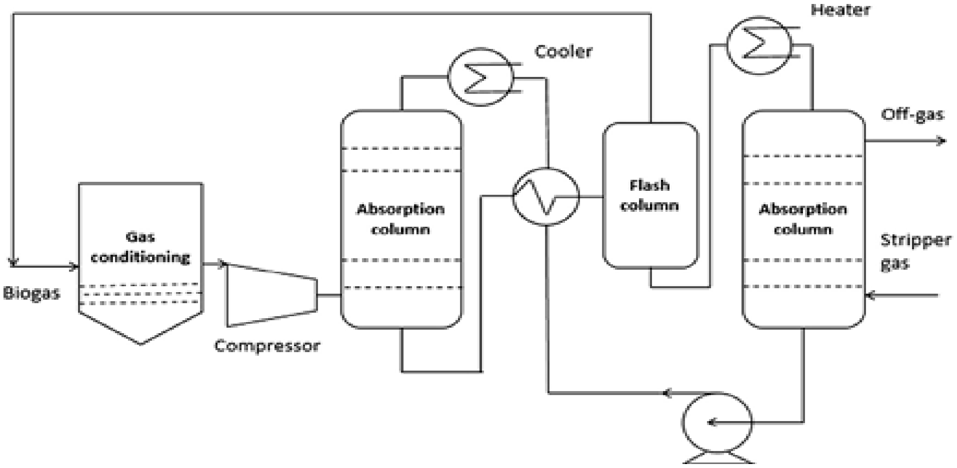


Fig 2.5 process flow diagram of physical absorption

2.5.5. Chemical absorption

Chemical absorption differs from physical absorption in the chemical reaction between absorbed substances and solvent. Chemical solvents tend to be favored over physical solvents when the concentration of CO_2 is low. Amines are widely used as a chemical solvent to absorb CO_2, as there are no CH_4 losses since the chemical solvent reacts selectively with CO_2. For example, an equipment supplier has reported CH_4 losses of only 0.1– 0.2% in a plant with a capacity of 300 N m^3/h (raw gas) [41]. However, simulations show quite different results, namely that more than

4% of CH_4 can be lost due to the dissolution of CH_4 in water [42]. These losses of CH_4 further affect the purity of CO_2 stream, which contains about 93% CO_2 and 6% CH_4. Another downside of this technology relates to energy consumption, as a large amount of high temperature heat is needed to regenerate chemical solvents.

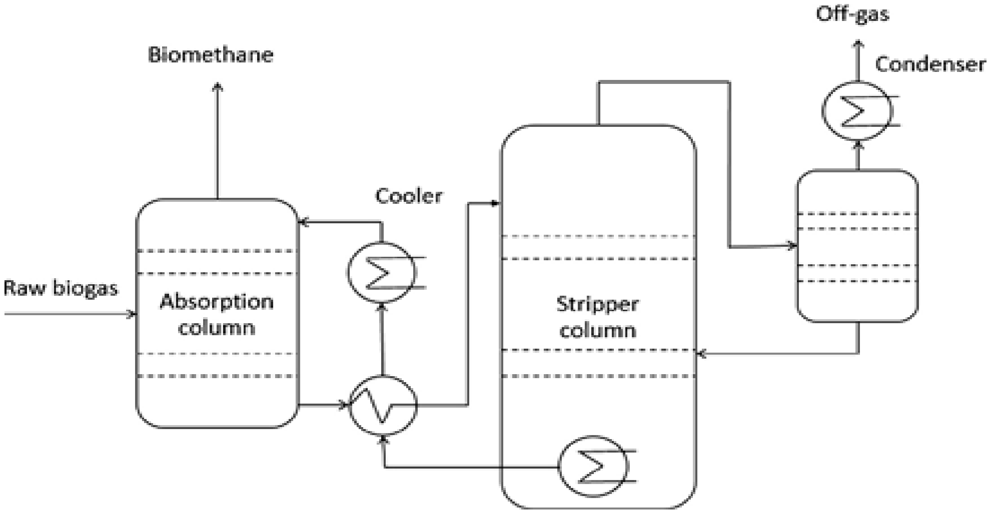


Fig 2.6 process flow diagram of chemical absorption

2.5.6. Membrane technology

Membrane technology is a separation method at molecular scale, and it has a number of merits, including low cost, energy efficiency and easy process. For biogas upgrading, CO_2 and H_2S pass through the membrane to the permeate side, while CH_4 is retained on the inlet side. Since some CH_4 molecules may also pass through the membrane, achieving a high purity of CH_4 involves large losses of CH_4. Basu et al and Scholz et al. [43]. Reviewed membrane-based technologies, which have been commercially applicable to biogas upgrading. Polyimide and cellulose acetate-based membranes were found to be the most suitable commercial membranes for biogas separation and enrichment for biogas separation. The optimal processes can deliver a CH_4 purity of 98% with recovery of 99%. For state-of-the-art membrane technologies, the electrical energy consumption for biogas upgrading is around 0.3 kW h/m^3.

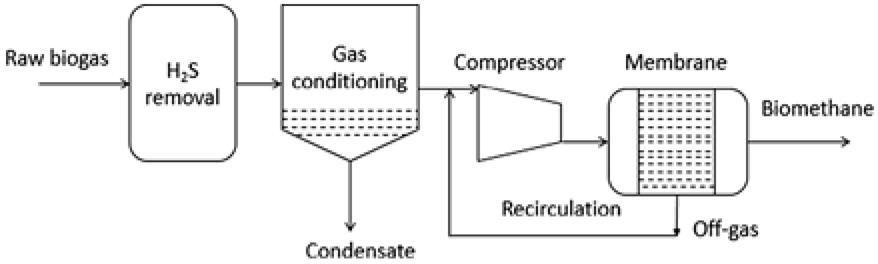


Fig 2.7 process flow diagram of chemical absorption

2.6. Adsorption techniques

Adsorption techniques are used in the chemically and physically adsorption process. Generally, the adsorption process can dehumidify gas, eliminate the odor or pollutants from the stream, or recover valuable solvent vapors from the stream. The adsorption process can penetrate the compound in liquid or gases into pores solid material (adsorbent). The gas or liquid compound adsorbed in the process is called adsorbate. For adsorption, gas should be non-combustible or difficult to burn, and the recovered pollutants should be valuable and diluted. chemicals, such as diluted NaOH solution, $FeCl_2$ solution, and $Fe(OH)_3$, were also used in H_2S removal and CO_2. The operating parameters such as flow rate, concentration and temperature had tested to determine the H_2S and CO_2 absorption efficiency.

2.6.1. Adsorption via Activated Carbon

The adsorption through activated carbon has been frequently investigated by researchers because the activated carbon has high surface area, porosity, and surface chemistry [47]. Moreover, this method is a cheap adsorbent that is widely used in the air pollution technologies. The activated carbon can be used and result in high adsorption capacity and fast reaction kinetic even in ambient temperature. Activated carbon is divided into impregnated and unimpregnated Types.

The impregnated activated carbon refers to the addition of cations to assist as catalyst in the adsorption process [48]. This impregnated activated carbon has the highest capability in removing H_2S compared with unimpregnated activated carbon. The unimpregnated activated carbon is a weak catalyst, and the rate is limited by complex reaction. Unimpregnated activated carbon is more interested in the oxidation of sulfide ion (HS^-) to the elemental sulfur. This unimpregnated activated carbon is dissociated with water film at the carbon surface

Several caustic compounds like sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium bicarbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3), potassium iodide (KI), or potassium permanganate ($KMnO_4$) are added as cations in impregnated activated carbon. In the study of Bagreev and Bandosz (2002), the highest added amount of NaOH in the impregnated activated carbon increases the H_2S removal capacity.

2.7. Purification

The purification unit consists of the following units

2.7.1. CO_2 separation Unit

The raw biogas is first passed through a CO_2 separation unit. The CO_2 removal takes place in an absorbing column by chemical absorption with an amines aqueous solution. The chemical reaction needs to form a weak intermediate compound so that the absorbent may be regenerated. To apply regeneration a pressure reduction or an increase in temperature is required. The solvent can be ammonia, different amines, or a mixture of amines and or NaOH solution.

2.7.2. H_2S separation Unit

Hydrogen sulphide is removed by using Impregnated activated carbons are carbons to which a solid chemical that has been mixed with carbon substrate before, during, or after activation. To improve their performance, activated carbons are often modified or uses a catalyst like sodium hydroxide (NaOH), potassium hydroxide (KOH) during the cleaning process.

2.7.3. Moisture separation units

Adsorptive drying means that H_2O is adsorbed on the surface of a drying agent. Silica gel, aluminum or magnesium oxides are such examples (Hagen et al., 2001). The drying agent is packed in containers and the moist gas is distributed in the drying bed. Normally an adsorption drier has two containers that are switched. While one will be drying and the other is being regenerated. Silica gel crystals should be replaced after a specific time according to the rate of purification. The capacities of the scrubbing units are decided according to the size of the biogas.

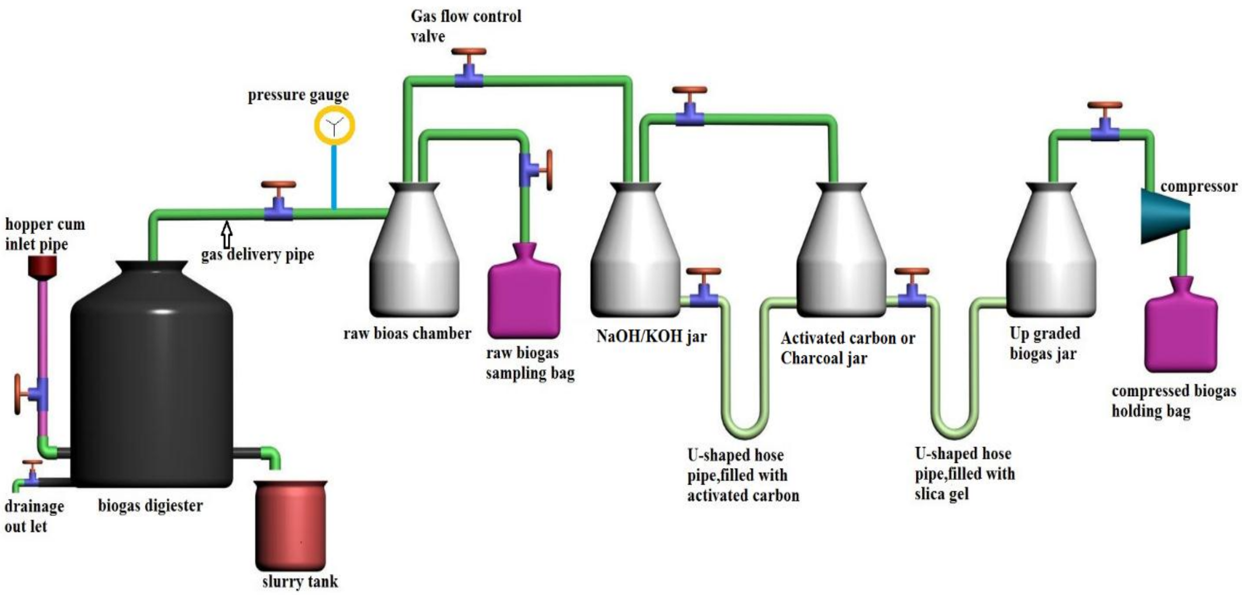


Fig 2.8 3D Max -Model of biogas upgrading processes (source Shuichi Torii, 2015)

CHAPTER THREE

3.1. Material and Methods

An extensive survey and analysis of different literature upgrading technologies was carried out to select the most appropriate starting point for the modeling and simulation, developing the suitable gas cleaning process, according to the specified requirement flow diagram of activated carbon, NaOH, amine solution and silica gel-based upgrading technology.

It is observed from the literature that the chemical absorption method uses aqueous chemical solution (NaOH solution, KOH, activated carbon and silica gel). The precipitates of aqueous chemical solution formed at the bottom of the scrubber reduce the performance of the system. Hence it is necessary to solve this problem by removing the chemical solution after the experimental work is conducted through the bottom out let valve of the chemical scrubber. So, it is proposed to use aqueous solutions of NaOH and KOH chemicals in chemical absorption method for purification of biogas.

The aim of this research was to develop and improve the quality of biogas produced from food wastes by using basic chemical scrubbers. The scrubbers are a system modeled to improve the quality of biogas by using chemical absorption and This treatment system is effective in eliminating carbon dioxide, hydrogen sulfide, and removal of vapor.

The computer program of aspen plus includes a library of standard unit operation blocks (e.g. pumps, heat exchangers, reactors, splitters), which represent processes taking place in an actual chemical plant. The simulation of a process plant is done by specifying configurations of unit operations and the flow of material, heat and work streams. an extensive components database containing physical properties of a large number of pure components Within the program there exist mathematical routines (convergence algorithms) for solving different equations of material and energy balances as well as equilibrium equations.

Different input categories were required to be filled into the program to conduct the simulation. These input categories are temperature and pressure of raw biogas, selecting reaction block specification, concentration in volume of adding chemicals, specific reaction between the chemicals and impurities, operating pressure and temperature of pumps, compressors and reacting blocks and simulation condition specification.

To be able to construct a process model in a flow sheet program the following three steps are necessary:

- *Flow sheet definition*: - all inlet streams to the system have to be defined as well as different unit operations and their interconnecting streams. The flow sheet also indicates all outlet (product) streams.
- *Chemical components:* - all chemical components in the system, from reactants to intermediates and products must be specified.
- *Operating conditions:* -the operating conditions, such as temperature, pressure, heat duties etc., for every unit operation must be specified. All input streams have to be completely defined.

3.2. Importance of H_2S And CO_2 Removal

For natural gas transportation over a wide range and long distance there are strict requirements for the gas quality. Acid gas removal units, often called gas sweetening are implemented in different industrial plants because of product specification and strict emission requirements. Being able to remove H_2S and CO_2 simultaneously from the gas is a crucial part of the process for reaching transportation specifications for rich gas. Rich gas is commonly used as a term for gas leaving an offshore facility and sent for further processing. H_2S is toxic and reacts to form weak acids in aqueous solutions, which are corrosive. The latter is also the case for CO_2. The rate of corrosion in equipment depends on processing temperature, amount of water and what type of chemicals that are used. For acid gas removal, absorption is widely applied by utilizing amines, NaOH and Activated Carbons, which vary in corrosiveness.

Combustion of biogas containing H_2S produces sulfur dioxide (SO_2). When SO_2 combines with water vapor, it produces sulfuric acid (H_2SO_4). This H_2SO_4 can damage exhaust pipes of engines, valves etc. by corroding them. If engine is run using biogas containing H_2S, its operating time period to the first routine overhaul may decrease by 10 to 15%. The gaseous SO_2 also dissolves in engine oil causing the oil to become acidic and lose its ability to lubricate, damaging the engine and shortening time between oil changes

Presence of CO_2 in biogas can result into problem of freezing at metering points and valves due to ice formation. Since carbon dioxide does not liquefy and tends to form dry ice upon compression, storage of biogas in medium pressure tanks would produce lumps in the compressor

Gas cleaning processes for removal of sulfur compounds, such as H_2S and CO_2, and generally as well as other compounds of halides and nitrogen compounds are most readily performed by means of a physical and chemical washing process at plant scales larger than approximately 20 MW_{fuel} [44]. In a physical and chemical process, the gas is washed with a suitable solvent, physical or chemical, in a packed (structured or unstructured) column or tray column at a temperature where the impurity absorption is efficient. Physical solvents tend to be favored over chemical solvents when the concentration of acid gases or other impurities is very high. The regeneration of chemical solvents is achieved by the application of heat, whereas physical solvents can often be stripped of impurities by reducing the pressure without

the application of heat. The absorption loading capacity for a physical or chemical solvent is proportional to the volumetric gas flow rate or the removed acid gases, respectively [44]. The solvent used with the absorbed AG (Acid Gas) and other impurities is transferred to a regeneration unit for purification and release of the acid gases.

General criteria for selection of the appropriate AG removal process configuration are among others given by: -

- the demand of the required gas purity
- the raw gas composition

A suitable solvent is essential for an efficient process to optimize the removal of undesired components while not removing desired components of the gas. typical solvents for chemical removal of AG and humidity are amines (Methyl diethyl amine (MDEA)), NaOH, silica gel and activated carbon.

3.3. Anaerobic Acidogenesis Of the Food Waste

A bench scale experimental study was conducted in a 10m^3 PVC ROTO reactor equipped with a water jacket heating system for maintaining a constant temperature of 37°C (mesophilic bacteria reaction). The pH was continuously controlled and maintained at pH=6.5, by injection of a buffer solution of 1 M sodium bicarbonate and 1 M sodium hydroxide. Stirrer blade provided continuous mixing of the material in the reactor. The reactor was operated in batch mode for four weeks. The feedstock to the reactor was food waste from the campus restaurant, consisting of mixed cooked and fresh food leftovers. Fresh feed material was prepared once a week and was stored at 4°C. The preparation included homogenization in a kitchen blender, diluting with water and sampling for further analyses.

3.4. Interactions between different microbial in the AD reactors

Reactions that occur are as follows as referenced in the Environmental Microbiology (Ralph & Dong 2010): -

Conversion of propionate to acetate: -

$CH_3CH_2COO^- + 3H_2O \leftrightarrow CH_3COO^- + H^+ + HCO_3^- + 3H_2$ (free energy value: +76.1 kJ) ………. (3.1)

Conversion of butyrate to acetate: -

$CH_3(CH_2)_2COO- + 2H_2O \leftrightarrow 2CH_3COO^- + H^+ + 2H_2$ (free energy value: +48.3 kJ) …………. (3.2)

In particular, hydrogen is the most important intermediate and the hydrogen-scavenging reaction makes the whole reaction energetically feasible. The following reactions occur as referenced in the Environmental Microbiology (Ralph & Dong 2010)

Acetogenic reactions: -

$2HCO_3^- + 4H_2 + H^+ \leftrightarrow CH_3COO^- + 4H_2O$ (free energy value: −104.6 kJ) …………………. (3.3)

$CH_3COO^- + H_2O \leftrightarrow CH_4 + HCO_3^-$ (free energy value: −31.0 kJ) …………………..……. (3.4)

$4H_2 + HCO_3^- + H^+ \leftrightarrow CH4 + 3H_2O$ (free energy value: −135.6 kJ) ……………….….……. (3.5)

Therefore, the methanogensis is the rate limiting step in the anaerobic digestion reaction and requires retention time of at least 15- 20 days for a steady state system as referenced in the Environmental Biotechnology: Principles and Applications.

3.5. Instruments and Chemicals Used

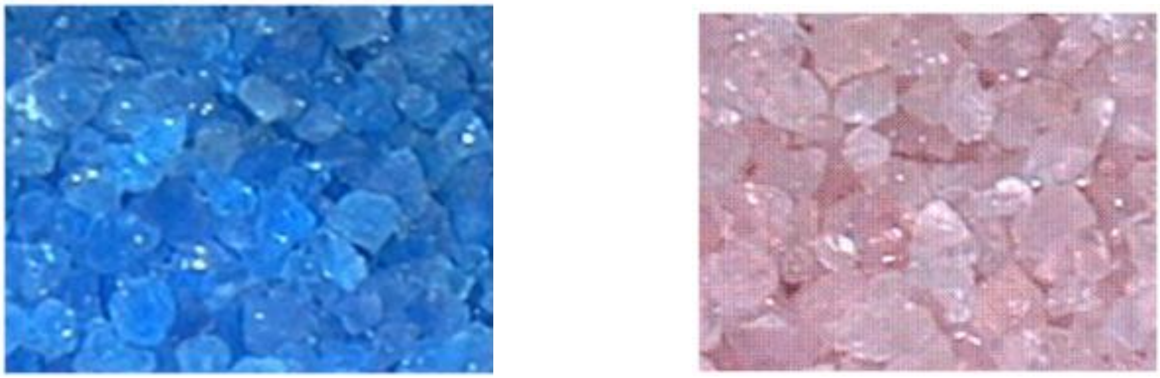
Gas Analyzer: used to measure the chemical composition of the biogas produced in the form of methane (CH_4), carbon dioxide (CO_2), oxygen (O_2), hydrogen sulfide (H_2S) and ammonia NH_3.

Fig 3.1. Gas Analyzer Model BIOGAS 5000

Air bags**: -** holds the biogas produced from the food waste anaerobically

Fig 3.2 air holding bag

Chemicals used: - for upgrading process chemicals which is used in the process are NaOH, Activated Carbon, KOH, granular silica gel and wood charcoal.



The fist colour of silica gel After absorbing the moisture, it is change to pink

Fig 3.3 chemicals used in biogas upgrading process

LPG cylinder: -LPG Gas cylinders have for many years been manufactured from metal (mainly steel with a small proportion from aluminum) in different sizes and with different valve types.

Fig 3.4. biogas LPG cylinder

Compressor: -is an equipment used to compress the biogas which is produced in the digester and the upgraded biogas in order to minimize space requirements.

Fig 3.5 compressor

PH meter: -used to measure the PH level of the gas which produced

Fig 3.6 PH meter

Pressure gauge: -used to measure the initial pressure of gas produced from the digester and during a compression process

Fig 3.7 pressure gauge

3.6. Parameters Affecting the Anaerobic Digestion of Food Waste

3.6.1. PH value

The pH value of the reacting material is a pivotal factor in the AD of food waste. The importance of the pH is due to the fact that methanogenic bacteria are very sensitive to acidic conditions and their growth and methane production are inhibited in acidic environment. Although it has been proven that the optimal range of pH for obtaining maximal biogas yield in anaerobic digestion is 6.5–7.5, the range is relatively wide in the plants and the optimal value of PH varies with substrate and digestion technique (Liu et al. 2007). The maximum energy recovery of MSW (municipal solid waste) can be obtained by using optimization control of PH. This model includes all three processes occurring in the AD system and is described as a set of algebraic equations that have been formulated based on mass balances for substrates, products and microbial components, and physic-chemical equilibrium relationships among ionized/unionized species.

The expression of relationship between pH and methane yield is (Liu et al. 2007): -

$$\frac{dCH_4}{dt} = (Vm_{max} X_m \frac{A_c^{-1} \times 10^{-PH}}{A_c^{-1} \times 10^{-PH} + K_a K_m}) \times (\frac{K_{im} a}{K_{im} K_a + A_c^{-1} + 10^{-PH}}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.6)}$$

Where: -

Vm_{max}= is the maximal yield rate of methane (in volume at 0°C and 1 atm pressure) per gram of methanogenic bacteria per day (L/g d);

X_m=methanogenic biomass (g/L);

K_m=saturation constant of methane yield (g/L);

K_{im}=inhibition constant of acetate on methane yield (g/L)

K_a=the dissociation constant for acetate (1.728×10^{-5})

A_c^{-1}=ionized acetate concentration (g/l)

3.6.2. Composition of food waste

The research first investigated the influence of the feedstock taken by the cafeteria food waste on the composition of the biogas. Samples of the slurry from the digesters were collected and analyzed for the TS and VS.

The composition of food waste is variable depending on the time of the year, cultural habit, regions etc.it is important to know the composition of food waste in in order to be able to predict both the biomethaniztion potential and the most efficient AD facility design. The biomethaniztion of the waste depends on the concentration of the four main components: protein, Lipids, carbohydrate and cellulose. This is due to the different bio-chemical characteristics of these components (Neves et al. 2007). The highest methane yields have systems with excess of lipids but with the longest retention time. The methanization is the fastest in the system with the excess of proteins followed by the reactors with excess of cellulose and carbohydrates respectively.

3.6.3. Loading rate

is the measure of the biological conversion capacity of AD system. It determines the number of volatile solids feasible as an input in the AD system. Overloading of the system can result in low biogas yield. This happens due to the accumulation of inhibiting substances such as fatty acids in the digester slurry (Vandevivere et al. 1999).

Loading rate can be calculated using the following equation: -

$$\text{Loading rate}\left(\frac{mgCOD}{m^3 * day}\right) = \frac{organic\ matter\left(\frac{mg\ COD}{m^3}\right) \times flowrate\left(\frac{m^3}{day}\right)}{operation\ volume(m^3)} \quad \ldots\ldots\ldots\ldots (3.7)$$

3.6.4. Retention time

retention time (residence time), in the AD reactors, refers to the time that feedstock stays in the digester. It can be calculated using the following equation:

$$\text{Retention time (days)} = \frac{operating\ volume\ V(m^3)}{flow\ rate\ Q\ \left(\frac{m^3}{day}\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.... (3.8)$$

3.7. Determination of Total Solids

The analysis of total solids (TS) was performed as stipulated in the standard method for the analysis. This was to determine the TS content which is the sample residue left in a testing crucible after evaporation of the digesters sample.

The equipment and apparatus for the TS test included: -

- Porcelain evaporating crucibles
- Analytical balance with sensitivity capable of weighing 0.01 gm.
- Drying oven for evaporating at 105 °C
- Desiccator and desiccant that contains a color indicator for moisture content
- Metal tongs
- Heat resistant gloves
- Muffle furnace

The calculations of the TS were performed based on the following equation: -

$$\mathrm{TS} = \frac{(A-B)}{(D-B)} \times 100\% \quad \text{.......} \quad (3.9)$$

Where: - A = weight of dish + dry sample

B = weight of dish

D = weight of dish + wet sample

Fig 3.8 Food waste from cafeteria

1st stage homogenization – chopping using food processor

2nd stage homogenization – blending using food liquidizer

Fig 3.8 sample preparation

3.8. Determination of Volatile Solids

After determining the TS, the respective cooled oven dried samples were put in crucibles. The crucibles were then placed in a muffle furnace and the content ignited at 550 °C for 15 to 30 minutes according to (Alpha, 2005 standards). By incineration at this temperature all the organic substances are burned, leaving only the inorganic ashes in the crucibles. The oven was switched off for about 10 minutes to allow the ashes to cool. The cooled samples were then removed and put in desiccators for an hour. The samples were then weighed together with the crucible in a sensitive analytical measuring balance. By subtracting the water content and the amount of organic ashes from the total weight of the material, the amount of VS in the sample was calculated.

$$VS=\frac{(A-C)}{(A-B)}\times 100\% \quad \text{.......} \quad (3.10)$$

Where A = weight of dish + dry sample

B = weight of dish

C = weight of dish + sample after ashing

two samples were taken and all two of them are mixture of the six food waste samples which are Injera, Rice, Pasta with macaroni, bread, vegetable, injera with meat.

Table 3.1 Total solid and volatile solid of the food waste

Food waste TS and VS						
Description	Crucible wt. (g)	Crucible + sample wt.(g)	Crucible + Sample Wt.(g) at (105^{o}C)	Crucible +Sample Wt.(g) at (550^{o}C)	TS (%)	VS (%)
Mixture A	48.51	94.99	62.33	48.99	29.73	88
Mixture B	48.91	99.40	64.53	49.43	30.93	89
Average	48.71	97.195	63.43	49.21	30.33	88.5

3.9. System Consideration

The study focuses on the development of an efficient gas cleaning and upgrading process for removing the impurities like H_2S, water and CO_2. based on this amount of chemicals consumed for chemical purification process was conducted in the MATLAB simulation software.

3.10. Modeling and Block Flow Diagrams

an extensive survey and analysis of absorption and adsorption-based technologies was carried out to select the most appropriate starting point for the modeling, simulation and developing the suitable gas cleaning process, according to the specified requirement of the biogas.

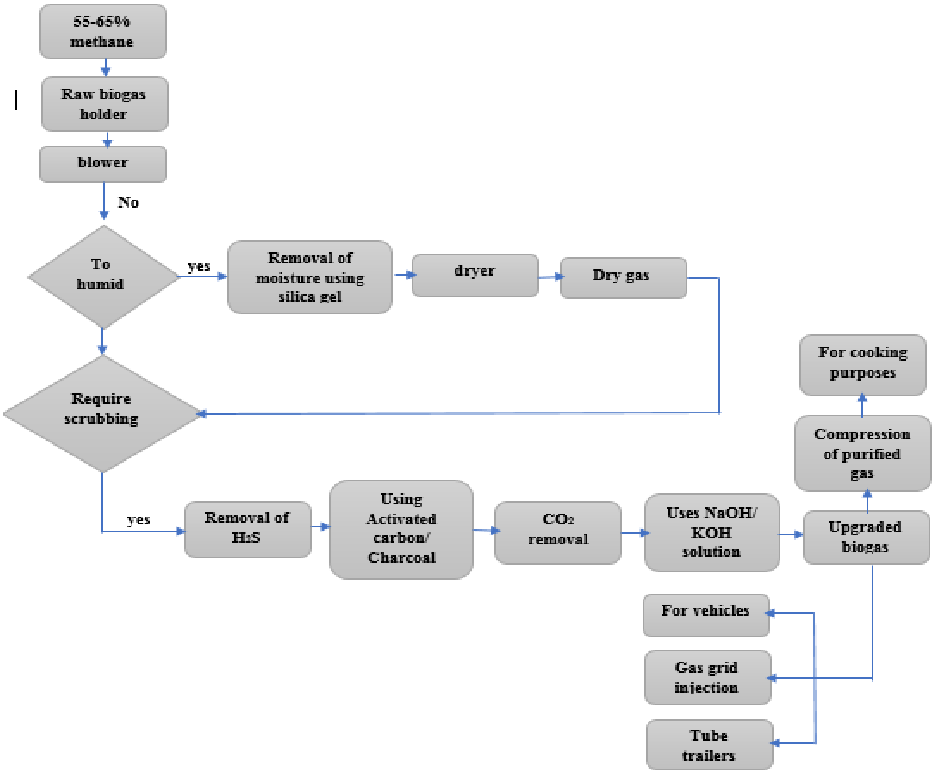


Fig 3.9 block flow diagram of the upgrading process

3.11. Elemental analysis of food waste

The estimation procedure and the biogas production process involve braking down of food waste into its elemental compositions, C, H, O, N, and S.

Table 3.2 Elemental analysis of food waste

FW Elemental Composition	In **%**
C	45.405
H	7.655
O	42.915
N	3.945
S	0.4

3.12. Material Preparation and Mathematical Modeling of Biogas Production

3.12.1. Material preparation

Three organic wastes (The digestion feed stock, namely cafeteria waste (CW) including vegetable wastes (VW), and fruit wastes (FW)) were collected from Addis Ababa university (sidist kilo campus) and the cattle manure was collected from a district near Addis Ababa university as a starter before using the food waste. Then all the substrates which are collected were crushed into small pieces of 2mm sizes with mechanical blender. The blended sample was mixed with equal proportion CW: VW: FW (1:1:1:1) and diluted in tap water in a ratio of 1:1. The prepared stocks were fed to a volume of 10m^3 biogas digester.

3.13. Mathematical Modeling of Biogas Production

The rate of change of any soluble or particulate substances (S$_i$ or X$_i$) in the liquid volume of the digester is given by the following: -

Total= inflow-out flow+ accumulation

$$\frac{dS_{liq,i}}{dt} = \frac{q_{in}S_{in,i}}{V_{liq}} - \frac{q_{out}S_{liq,i}}{V_{liq}} + \sum_{j=1-19} p_j V_{i.j} \quad \text{………………………..………… (3.11)}$$

Where $p_j = the$ kinetic rate for process (kg COD /m^{3}day)

$V_{i.j}$= is the stoichiometric coefficient of component i at process j

$S_i =$ is the concentration of component i (kgCOD /m^3)

$q_{in}q_{out}$ =are the inflow and out flow, m^3/day

$V_{liq} =$ the volume of the reactor (m^3)

The gas phase rate equations are described with only dynamic state components (assuming a constant gas volume).

$$\frac{ds_{gas,i}}{dt} = -\frac{q_{gas}s_{gas,i}}{V_{gas}} + p_{T,i}\frac{V_{liq}}{V_{gas}} \quad \text{…………………………………………………… (3.12)}$$

Where $s_{gas,i}$=concentration of gas, i (Kmole/m^3)

q_{gas}=is the gas flow (m^3/day)

V_{liq}, V_{gas} =is the volume of reactor and head space (m^3)

$p_{T,i}$=is the transfer rate of gas i, (Kmole/m^3 day)

The buildup of methane and CO_2 through anaerobic digestion was 1st described using stoichiometric approach by Buswell in 1936 (Buswell and Hatfield 1936);

The water vapour content of the biogas is calculated, and from this the dry gas volume

obtained,

$$V_{tr,N} = V \times \frac{(p-p_w)\times T_N}{p_N \times T} \quad \text{(3.13)}$$

$V_{tr,N}$ =volume of the dry gas in the normal state, in ml_N

V =volume of the gas as read off, in ml

p = pressure of the gas phase at the time of reading, in kPa

p_w = vapour pressure of the water as a function of the temperature of the ambient space, in kPa

T_N = normal temperature; T_N = 273 K

p_N = normal pressure; p_N = 1.01325 bar

T = temperature of the fermentation gas or of the ambient space, in K

If the methane content is measured in the humid gas instead of the dry gas, the methane content of the dry gas can be calculated as follows

$$C_{CH_{4,tr}} = C_{CH_{4,f}} \times \frac{p}{p-p_w} \quad \text{(3.14)}$$

$C_{CH_{4,tr}}$ =methane volume fraction in the dry gas, in %

$C_{CH_{4,f}}$ = methane volume fraction in the moist gas, in %

p = pressure of the gas phase at the time of reading, in hPa

the measured concentrations of the biogas components will need to be subjected to headspace correction since inert gas in the headspace at the beginning of the fermentation test causes a dilution of the biogas components. The corrected concentrations can be calculated by means of the following Equation

$$C_{tr,korr} = C_{tr,t2} + (C_{tr,t2} - C_{tr,t1}) \times \frac{V_K}{V_{BG}} \quad \text{(3.15)}$$

$C_{tr,korr}$= corrected concentration of the biogas components in the dry gas, in %

C_{tr}= measured concentration of biogas components in the dry gas, in %

V_K = the headspace volume, in ml

V_{BG}= volume of the biogas produced, in ml

t = time of measurement ($t_2 > t_1$)

If the volume fractions of principal components of the biogas produced are analyzed simultaneously

$$C_{tr,korr} = (C_{CH_4(CO_2)}) + (C_{CH_4(CO_2)} - C_{CH_4(H_2S)}) + C_{CH_4(CO_2)} - C_{CH_4(H_2O)} \times \frac{100}{C_{CO_2} + C_{H_2S} + C_{H_2O}} \quad (3.16)$$

$C_{tr,korr}$= corrected concentration of the biogas components in the dry gas, in %

$C_{CH_4(CO_2)}$= measured concentration of methane (or carbon dioxide) in the gas, in %

$C_{CH_4(CO_2)} - C_{CH_4(H_2S)}$=measured concentration of carbon dioxide in the gas minus measured concentration of hydrogen sulfide in the gas, in %

$C_{CH_4(CO_2)} - C_{CH_4(H_2O)}$= measured concentration of carbon dioxide in the gas minus measured concentration of water in the gas, in %

C_{CH_4} = measured methane concentration in the gas, in %

C_{CO_2}= measured carbon dioxide concentration in the gas, in %

C_{H_2S} = measured hydrogen sulfide concentration in the gas, in %

C_{H_2O} = measured water concentration in the gas, in %

Mathematical algorithm of a biogas digester is described as: -

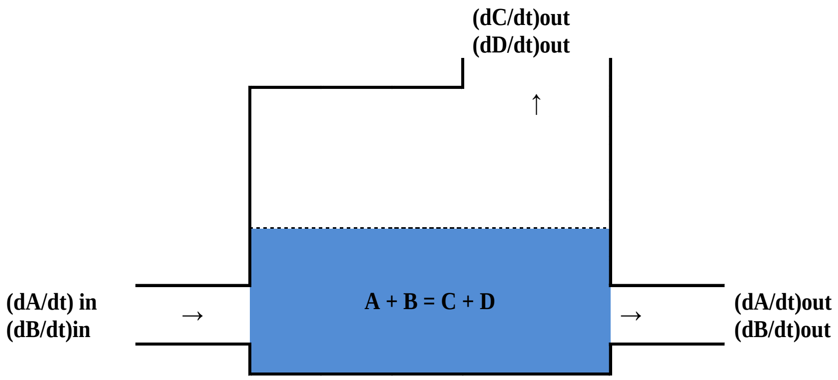


Fig 3.10 mathematical modeling of biogas digester

3.13.1. Differential equations

The rate of accumulation of each component in the reaction can be described by a mathematical differential equation. For instance, the rate of change of concentration of "A" in the tank is equal to the rate of change of concentration due to new feedstock being added plus the rate of change of concentration due to material going to outlet plus the rate of change of concentration due to the biochemical reaction. The set of differential equations that follows from the simple equation is given below

$$\frac{d[A]}{dt} = \frac{d[A]}{dt_{in}} - \frac{dA}{dt_{out}} - K[A][B]^{C_1} \quad \text{(3.17)}$$

$$\frac{dB}{dt} = \frac{d[B]}{dt_{in}} - \frac{d[B]}{dt_{out}} - C_1K[A][B]^{C_1} \quad \text{(3.18)}$$

$$\frac{dC}{dt} = \frac{d[C]}{dt_{in}} - \frac{d[C]}{dt_{out}} + C_2K[A][B]^{C_1} \quad \text{(3.19)}$$

$$\frac{dD}{dt} = \frac{d[D]}{dt_{in}} - \frac{d[D]}{dt_{out}} + C_3K[A][B]^{C_1} \quad \text{(3.20)}$$

The reaction rate constant k can be either determined experimentally or taken from literature. Theoretically, we can determine k from the Arrhenius equation

$$K = Ce^{-E_A/RT} \quad \text{(3.21)}$$

For an initial approximation, Wu et al gives an estimation of the value of k

$$K = 6.21 \times 10^{-8} \left(\frac{mol}{l} \times t\right)^{-1} \quad \text{(3.22)}$$

The value of k used in this model is determined by matching the model to the experiment initially and more accurately by running a number of simulations.

$C_aH_bO_c$+ (a $-\frac{b}{4}-\frac{c}{2}$)$\mathrm{H_2O} \rightarrow (\frac{a}{2}+\frac{b}{8}-\frac{c}{4})\mathrm{CH_4} + (\frac{a}{2}-\frac{b}{8}+\frac{c}{4})\mathrm{CO_2}$ ……................. (3.23)

Then the equation was modified by Boyle in 1977 (Boyle 1977) to represent also NH_3 and H_2S formation (Deublein and Steinhauser, 2011);

$\mathrm{C_nH_aO_bN_cS_d + YH_2O \rightarrow XCH_4 + (n-x)CO_2 + cNH_3 + dH_2S}$ ………………............... (3.24)

Where

X=1/8(4n+a-2b-3c-2d) for CH_4 …………………………... (3.25)

Y=1/4 (4n-a-2b-3c+2d) for H_2O …………………………... (3.26)

$n-x = \frac{n}{2}-\frac{a}{8}+\frac{b}{4}+\frac{3c}{8}+\frac{d}{4}$ for CO_2 …………………….. (3.27)

C: n = x + (n-x) ……………………………………………………………………… (3.28)

H: a+2y=4x+3c+2d ………………………………...(3.29)

O: b+y = 2(n-x) ……………………………………………………………………… (3.30)

N: c=c ……………………………………………………………………………………(3.31)

S: d=d ……………………………………………………………………………...... (3.32)

Table 3.3 biogas production Balance of chemical reaction

	Left	right
C	n	x+(n-x) =n
H	$a+\frac{2}{4}(4n-a-2b-3c+2d)$ $2n-\frac{a}{2}-b-\frac{3}{2}c+d$	$\frac{4}{8}(4n+a-2b-3c-2d)+3c+2d$ $2n+\frac{a}{2}-b+\frac{3c}{2}+d$
O	$b+\frac{1}{4}(4n-a-2b-3c+2d)$ $\frac{b}{2}+n-\frac{a}{4}-\frac{3c}{4}+\frac{d}{2}$	$2[(n-\frac{1}{8}(4n+a-2b-3c-2d)]$ $n-\frac{a}{4}+\frac{b}{2}+\frac{3c}{4}+\frac{d}{2}$
N	C	c
S	D	d

3.14. Purification System

The purification unit consists 0.002m^3 volumes of three steel made cylindrical shape scrubber connected by 1cm pipe. The upgrading materials are NaOH/KOH, activated carbon/Charcoal, and silica gel was added to each purification unit to remove CO_2, H_2S and H_2O from the raw biogas. Some specific materials like ball gate valves, gas pipes, steel made scrubber, pressure gauge, gas flow meter analyzer, pH meter, are the Maine equipment's used, NaOH and granular silica gel of size 1-2mm was crushed manually into powder form to increase the surface area for absorbing CO_2 efficiently and water vapor respectively.

Fig 3.11 Raw biogas scrubbing set up

3.14.1. Initial Conditions taken Before upgrading for the produced biogas

- Biogas flow rate to the scrubber = 0.0865m^3/hr. (portable GAS analyzer GA5000)
- Inlet Temperature of biogas to the scrubber =27℃$(300k)$
- Working pressure of the scrubber = 1.025bar (Addis Ababa condition)
- Water content = 4.75%
- Biogas production rate = 0.425
- Composition of produced biogas from portable GAS analyzer GA5000 (CH_4 =64.3%, H_2S=10%, CO_2 =30%)
- Scrubber internal diameter: - 0.75 cm
- Scrubber external diameter: - 1.25 cm
- $V_{gas} = V_{init\ tank} - V_{waste} - V_{water} = V_{init\ tank} - \frac{mass\ of\ waste}{density\ of\ waste} - \frac{mass\ of\ water}{density\ of\ water}$

$$=10{,}000\text{L} - \frac{230kg}{\frac{1200kg}{l}} - \frac{1380kg}{\frac{1000kg}{l}} = 9998.41L = 9.9m^3$$

3.14.2. Absorption technologies

The absorption technique can either be physical or chemical H_2S absorption. In this case, the physical absorption has dissolved the trace components and is followed by chemical reaction of the trace component and solvents (common chemical solvent was used). Normally, physical absorption of H_2S occurs in water or organic solvent [45]. Kim et al. (2004) and Palmeri et al. (2004) stated that the chemical absorption benefits the efficiency, reaction rate, and the operation of H_2S removal compared with physical absorption (water scrubbing) [46]. Chemical absorption involves the formation of reversible chemical bonds between the solute and the solvent. In the chemical absorption, solvent itself undergoes regeneration, which involves bond breaking. Biswas et al. (1977) reported that the chemicals used in the process are (NaOH) and activated carbon. NaOH is part of the alkali oxide group. The other alkali oxides basically used in biogas upgrading process of technologies are $Ca(OH)_2$ and KOH.

3.14.3. Factors affecting the upgrading process via absorption

3.14.3.1. PH of the solvent

The pH of the solvent affects the absorption process and, therefore, the absorption rate. Addition of acid or base leads to low absorption rate. When KOH and NaOH were used, the optimum pH was found to be 13.3 and 12.9, respectively [49]. Ammonia and amines had the best pH value of 11.5-12 [50].

3.14.3.2. Concentration of the absorbent

Concentration plays an important role in absorption. Factors that affect the absorption include:

(I) gas loading rate,

(II) Increase in solution viscosity which decrease diffusion coefficient and absorption rate

3.14.3.3. Reaction temperature

Temperature is an important parameter of any chemical, biological, and physical reactions. Chemical absorption is influenced by temperature and the different absorbents behave differently at particular temperatures.

3.14.4. Mathematical modeling of biogas upgrading

Taking as a base case of the biogas production mathematical formula we develop a general algorithm of upgrading

Biogas production formulas: -

$A+B \rightarrow C + D$ …………………………………………………………………………… (3.33)

$C_nH_aO_bN_cS_d + YH_2O \rightarrow XCH_4 + (n-x)CO_2 + cNH_3 + dH_2S$ ………………………… (3.34)

And from this upgrading one becomes: -

$[C] + [E + F + G] \rightarrow H$ …………………………………………………………………… (3.35)

$aCH_4 + bNaOH + fC + gSiO_2 \rightarrow XCH_4 + YNa_2CO_3 + ZH_2O + PS + qO_2 + rH_4SiO_4$ ………… (3.36)

Table 3.4 biogas upgrading balance of chemical reaction

	Left	right
C	$a + f$	$x + y$ $x = a + f - y$ $x = a + f - \frac{b}{2}$
H	$4a + b$	$4x + 2z + 4r$ $z = 2a + \frac{b}{2} - 2x - 2r$ $z = 2f - \frac{b}{2} - 2r$
O	$b + 2g$	$3y + z + 2q + 4r$ $2q = b + r - 3y - z - 4r$ $2q = b - 3y - 3r - z$ $q = \frac{b}{2} - 4b - \frac{5}{2}r - f$
Na	b	$2y$ $y = \frac{b}{2}$
Si	$2g$	r

First order equation of produced methane: - $\frac{d[c]}{dt} = \frac{d[c]}{dt_{in}} - \frac{d[c]}{dt_{out}} - k[c][E][F][g]^{c_1}$………… (3.37)

First order equation of NaOH: - $\frac{d[E]}{dt} = \frac{d[E]}{dt_{in}} - \frac{d[E]}{dt_{out}} - C_1k[c][E]^{c_1}$………………………… (3.38)

First order equation of Activated carbon: - $\frac{d[F]}{dt} = \frac{d[F]}{dt_{in}} - \frac{d[F]}{dt_{out}} - C_2k[c][F]^{c_1}$ ……………… (3.39)

First order equation of Silica gel: - $\frac{d[g]}{dt} = \frac{d[g]}{dt_{in}} - \frac{d[g]}{dt_{out}} - C_3\, k[c][g]^{c_1}$ ……………………… (3.40)

First order equation of final product of methane: -$\frac{d[H]}{dt} = \frac{d[H]}{dt_{in}} - \frac{d[H]}{dt_{out}} - C_4 k[c][E][F][g]^{c_1}$ …... (3.41)

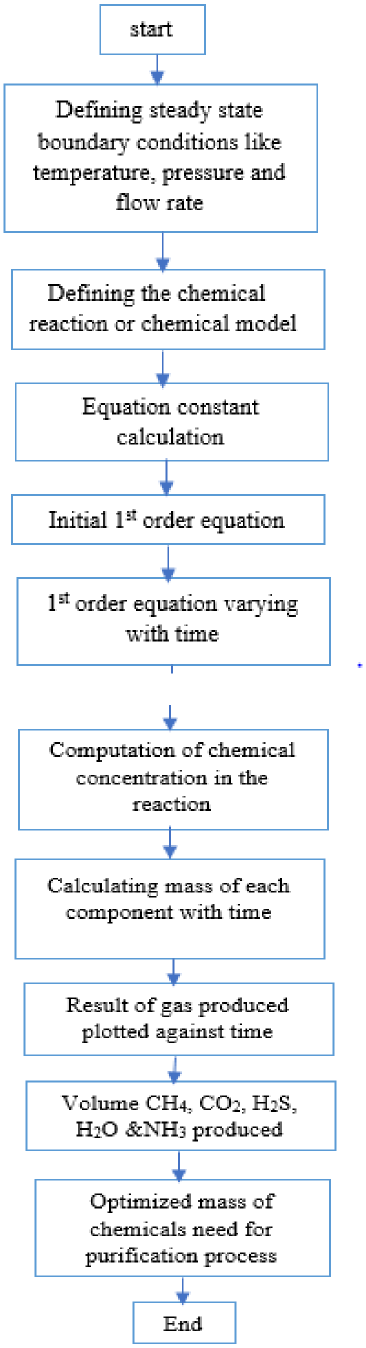


Fig 3.12 Biomethane production and its chemical consumption algorithm step in Matlab

3.15. Experimental Apparatus Setup

The design of experiments consists of four sections: a metabolism section to generate the desired biogas, raw gas sampling, a contaminants removal section to upgrade the biogas and the compressing and bottling analysis section.

During the study the experiment were operated batch wise with respect to absorption and adsorption phases.

1) The first one is metabolism section to generate the desired biogas (digester)
2) The raw gas collecting chamber and raw biogas sampling
3) The upgrading unit section (contaminant removal section)
4) storage/compression and bottling section

a) The upgrading section consists of three scrubbing cylindrical shaped metal made (0.002m^3). The first flask of the upgrading unit contains solution of NaOH which was varied from 1-10 kg per litter for CO_2 Removal experimental runs. the raw gas collection flask and the first purification sheet metal made scrubber was interconnected by 25mm diameter of 0.45cm long steel pipes and the cylindrical scrubber is 15cm long to remove CO_2 through NaOH solution. The biogas was passed through the upgrading first scrubber where it reacts with NaOH/KOH of 0.1 moles with a biogas flow rate of 0.0865m^3/hr. and the solution flow rate of 2.77m^3/hr, where found to yield high purity of methane. The chemical reaction during the process was: -

$$2NaOH_{(aqu)} + CO_{2\,(g)} \rightarrow Na_2CO_{3\,(aqu)} + H_2O_{(l)} \quad \ldots\ldots\ldots\ldots (3.42)$$

The carbon dioxide removal efficiency was calculated using: -

$$\eta_{co_2} = \left(1 - \frac{co_{2\,pure}}{co_{2\,raw}}\right) \times 100\% \quad \ldots\ldots\ldots\ldots (3.43)$$

b) For the adsorption of contaminants (H_2S and H_2O) enters (adsorption column) i.e. the second and third removal scrubber after passing the CO_2 capture trap and gas was transferred from CO_2 flask to H_2S removal flask. They are interconnected by 25mm diameter and 0.45cm long galvanized steel pipes. During removal process the steel pipes was filled with impregnated activated carbon was 10g per liter of water and NaOH (as catalyst to activate the reaction or as an oxidizing agent) and this reaction has the highest capacity in removing H_2S.this reaction is an adsorption process. The oxidizing agent still lingers on the carbon surface and changes its surface chemistry. The hydrogen sulfide is adsorbed on to the carbon surface and dissolution of H_2S into the water film is resulted. Finally, the dissociation of the hydrogen sulfide into ions, and is the surface reaction with oxygen functional group.

$2NaOH+H_2S \rightarrow Na_2S+2H_2O$ ………………………………………....................... (3.44)

$Na_2S + 2H2O + H_2S \rightarrow HS_2^- + H_3O^+ + 2NaOH$ …………………….………….......... (3.45)

HS_2^- (ads) + 2C(O*) (ads) → S_2 (ads) +OH^- ……………………………....…...... (3.46)

HS (ads) + 3C(O*) (ads) → SO_2(ads) +OH^- (side reaction) ……………………...... (3.47)

The l-shaped connected line was closed by using gas flow control valves in all connections.

c) Removal of H_2O in the galvanized steel pipe adsorption column was filled with a freshly prepared powder and granular form of silica gel for all runs. Silica gel as it has very good moisture absorbing capacity. The biogas enters the moisture eliminating column after passing the H_2S removal unit to ensure that the biogas was dry.as silica gel. NaOH and activated carbon material have significance H_2O and H_2S adsorbing capability, there for biogas flows through, these adsorbents from the one end to the other end of the pipes.

$2H_2O$ +Silica gel (SiO_2) → H_4SiO_4 ………………………………………………… (3.48)

Fig 3.13 Representative test set up

3.16. Chemical Reaction Kinetics of CO_2 Purification

The chemical reaction involved in CO_2 absorption in NaOH was listed as follow: -

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$ ………………………………………………………...... (3.49)

Which can be ionically represented as: -

$2OH^- + CO_2 \rightarrow CO_3^{2-} + H_2O$ ………………………………………………………… (3.50)

According to the steady-state principle to the intermediate zwitterion, the rate of reaction of CO_2 in the aqueous solutions can be expressed as: (Caplow 1968, Vaidya and Kenig 2007).

$r = \frac{R_1CO_2R_1NaOH/KOH}{1+\frac{K_{-1}}{K_B(B)}}$ …………..……………………………………………………………

(3.51)

Where $K_B(B)$ represents deprotonation of the zwitterion by bases including H_2O, OH^-, as well as mixture. When the rate of reverse reaction of zwitterion formation is much faster than deprotonation reaction, i.e. $K_B(B) << K_{-1}$ the reaction rate of CO_2 can be expressed as: -

$r_1 = \frac{k_1 k_B(B)}{K_1}$ (CO_2) (NaOH) /KOH…….. (3.52)

3.17. Mechanism of H_2S Removal

With a water-based mixture as the source in absence of air, the process follows the mechanism of the wet streams with no oxygen. The major reaction in hydrogen sulfide chemical adsorption involves the H_2S oxidation by oxygen to form elemental sulfur and water:

$2H_2S + O_2 \rightarrow S_2 + 2H_2O$ ……………………………………... (3.53)

HS_2^- (ads) + 2C(O*) (ads) → S_2 (ads) +OH^- ……………………………………………….. (3.54)

HS (ads) + 3C(O*) (ads) → SO_2(ads) +OH^- (side reaction) ……………………………….. (3.55)

The H_2S is adsorbed on the inner surfaces of modified activated carbon with defined pore sizes. In order to enhance the reaction rate and the total load, an investigation of H_2S oxidation rate has been provided by Klein and Henning (51). It Was summarized that the rate varies from 0-1 and from 0.5-1 in terms of O_2 and H_2S respectively at relatively low H_2S concentrations. The existence of a steady state was found by Sreeramamurthy and Menon (52). Several side reactions also occur on the carbon surface during H_2S oxidation, which produce sulfur compounds other than elemental sulfur.

For wet streams with no oxygen the following mechanism was proposed by Adib et al. (Adib Bagreev, and Bandosz,2000)

H_2S(gas) → H_2S (ads) ……………………………………………………………...…. (3.56)

H_2S(gas) → H_2S (ads-liq) ……………………………………………………….…. (3.57)

H_2S (ads-liq)→ HS^- (ads) + H^+ …………………………………………………….. (3.58)

$2HS^-$ (ads) + O (ads) →2S (ads) + H_2O ………………………… ……………………. (3.59)

where H_2S (gas), H_2S (ads-liq) and H_2S (ads) are concentration of hydrogen sulfide in gas, liquid film and adsorbed phases respectively. In step 1, the hydrogen sulfide is adsorbed onto the carbon surface, step 2 is the dissolution of hydrogen sulfide into the water film, step 3 is the dissociation of the hydrogen sulfide into ions, and step 4 is the surface reaction with oxygen functional group.

3.18. The Silica-Water Interface

The dissolution reaction

The silica polymorphs dissolve in water by the reaction

$SiO_2(s) + 2H_2O = H_4SiO_{4\,(aq)}$ ……………………………………………………… (3.56)

and the equilibrium constant for this reaction is

$$K = \frac{a_{H_4SiO_4}}{a_{SiO_2}a_{2H_2O}} \quad \text{……………………………………………………………………} \quad (3.57)$$

The fundamental reaction describing the kinetics of water absorption and silica dissolution including its precipitation is

$SiO_2 + 2H_2O = (*)^{\neq}$ ……………………………………………………………..... (3.58)

$(SiO_2\times 2H_2O) \neq= H_4SiO_4$ ……………………………………...… ……………………. (3.59)

and

$H_4SiO_4\,(*)^{\neq}$ …………………………………………………………………………… (3.60)

$(*)^{\neq}$ =SiO2 +2H2O ………………………………………………………………………… (3.61)

The $(*)^{\neq}$ indicates an activated intermediate species whose stoichiometry is unknown. At equilibrium, Reactions $SiO_2 + 2H_2O = (*)^{\neq}$ and H_4SiO_4 $(*)^{\neq}$ proceed at equal rates. From this basis, Rimstidt and Barnes (1980) derived an integrated rate equation which accounted for both reaction directions to determine that since

$r_+ = (dnH_4SiO_4/dt) + = Ak+ \, aSiO_2a^2H_2O$ ……………………….……………………....... (3.62)

and

$r- = (dnH_4SiO_4/dt)- = Ak- \, aH_4SiO_4$ …………………………………………………......... (3.63)

where nH_4SiO_4 is the number of moles of H_4SiO_4 ……………………………………… .. (3.64)

A = is the interfacial area in (M^2)

K+ and k- = are the dissolution and precipitation rate constants, respectively.

So, the net rate is

$R = (dnH_4SiO_4/dt) = A\,(k+ \, aSiO_2a^2H_2O - k- \, aH_4SiO_4)$ …………………………………….. (3.65)

Experimental dissolution rate data gives the reaction rate, rH_4SiO_4, for a population of water molecules that reacts per unit area of the silica surface. The apparent rate constant, k+ and rH_4SiO_4.are linked by recasting the net reaction rate in terms of the number of moles of water molecules per reactive area (mol M^{-2}) such that the reaction rate, rH_4SiO_4, is equal to the number of adsorbed H_2O molecules multiplied by the apparent rate. This gives

number moles of adsorbed H_2O per square meter = $X_{H2O} \times N_{t,\,ads}$

where X_{H2O} = mole fraction of sites accessible to water molecules

$N_{t,\,ads}$ = moles of reactive sites on the silica surface (mol M^{-2})

so that the rate is expressed

$r = X_{H2O} \times N_{t,\,ads}{}^{K'+}$ and the reaction rate is expressed as $K_+ = \frac{X_{H_2O}N_{t,ads}}{a_{SiO_2}((aH_2O)^\wedge 2}$ ……….. (3.66)

formulation of the rate constant, k_+, describing the frequency that an adsorbed water molecule binds to a silica surface to form an activated complex.

Fig 3.14 photo during experimental work

CHAPTER FOUR

4.1. Experimental Result and discussion

4.1.1. Absorption of CO2

The general purpose of this paper is cleaning system of biogas derived from food wastes and the cow manure is used as starter. The biogas was passed through the upgrading first cylindrical steel made scrubber where it reacted with $Na(OH)_2$ solution. In this case, aqueous solutions of $Na(OH)_2$ and KOH were used as chemical solvents to demonstrate and comparing which chemical solvent is the best of the ability to absorb CO_2. the first reactor flask was observed to remove a high portion of CO_2 gradually (approximately 80-85% removal efficiency) resulting in CH_4 enriched biogas. This alkali solution $(NaOH)_2$ fully controls CO_2 reaction in the biogas intensively through an acid-base neutralization reaction absorbing and reducing the desired gas. the average CO_2-concentration in the raw biogas was about 35.4%, whereas, the CO_2-concentration in upgrading gas decreased steadily with increasing of $Na(OH)_2$ and KOH concentration. some CO_2 simultaneously absorbed and reversibly bound on the surface of activated carbon and silica gel before come out from the scrubber.

Table 4.1 Experimental result on the concentration of CO_2 after purification

Chemical used	Quantity of chemical used	PH range	Time per experiment	CO_2concentration flow before removal	CO_2 concentration flow after removal
NaOH	1-10g	5-8.5	50min	35-34.89%	29-4%
KOH	1-10g	5-8.5	50min	36.55-34%	30-10%

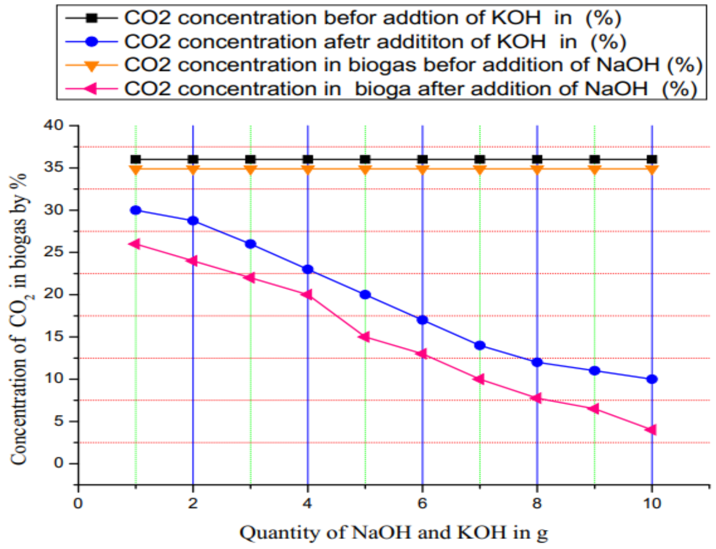


Fig 4.1. Experimental result of CO_2 Removal

Table 4.2 Literature result (source Shah Divyang R., Nagarsheth Hemant J. and Acharya Pradeep January 2016)

Chemical used	Quantity of chemical used	PH range	Time per experiment	CO_2concentration flow before removal	CO_2 concentration flow after removal
NaOH	1-10g	5-8.5	75 min	40%	29-1.25%
KOH	1-10g	5-8.5	75min	36.5%	33-5%

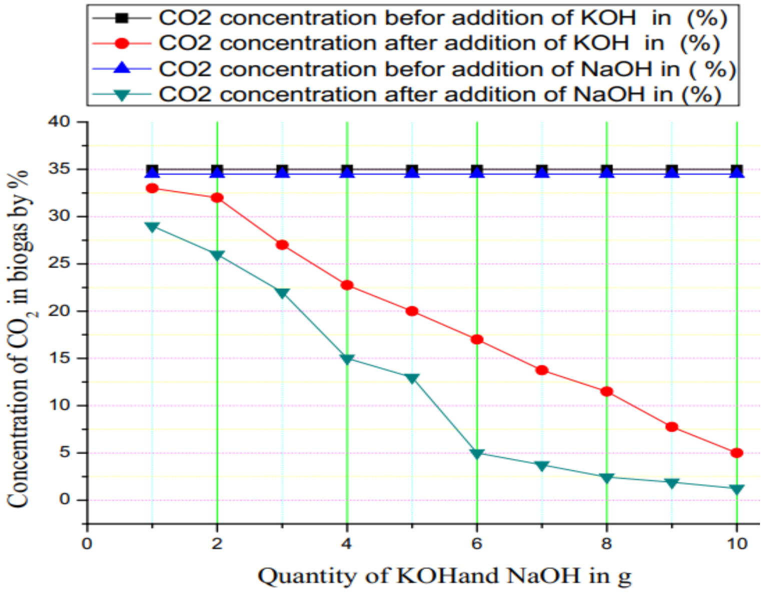


Fig 4.2. Literature result of CO_2 Removal

4.1.2. Removal of H_2S

The sulfide removal process is evaluated based on the selected Activated carbon. Tests were conducted with the controlled flow rate of biogas directly from the digester. The average H2S-concentration was varied 463 ppm and 477 ppm introduced into the scrubber. After adsorption, this concentration is gradually decreased based on the amount by up to 10-20 ppm variation when 10 g activated carbon is used. Due to its extremely porous form of carbon and thus it has a very large surface area available for adsorption of H2S. after passing these concentrations decreased steadily with respect to amount of these chemicals by 10 ppm and 55 ppm at 10 g usage of activated carbon.

Table 4.3 Experimental result on the concentration of H_2S after purification

Chemical used	Quantity of chemical used	PH range	Time per experiment	H_2S concentration flow before removal	H_2S concentration flow after removal
Activated carbon	1-10g	5-8.5	50min	477 ppm	350-35ppm
charcoal	1-10g	5.8.5	50min	463 ppm	400-95 ppm

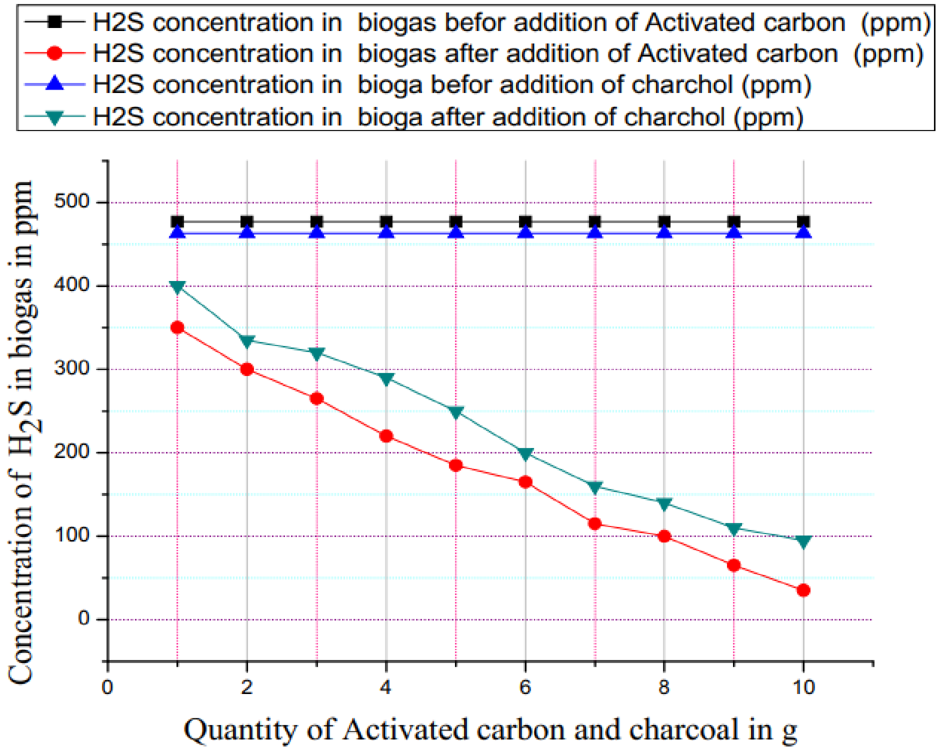


Fig 4.3. Experimental result of H_2S removal

Table 4.4 Literature result (source Muhammad Rashed Al Mamun and Shuichi Tori march 2017)

Chemical used	Quantity of chemical used	PH range	Time per experiment	H_2S concentration flow before removal	H_2S concentration flow after removal
Activated carbon	1-10g	5-8.5	75min	495ppm	350-12ppm
charcoal	1-10g	5.8.5	75min	490ppm	400-35ppm

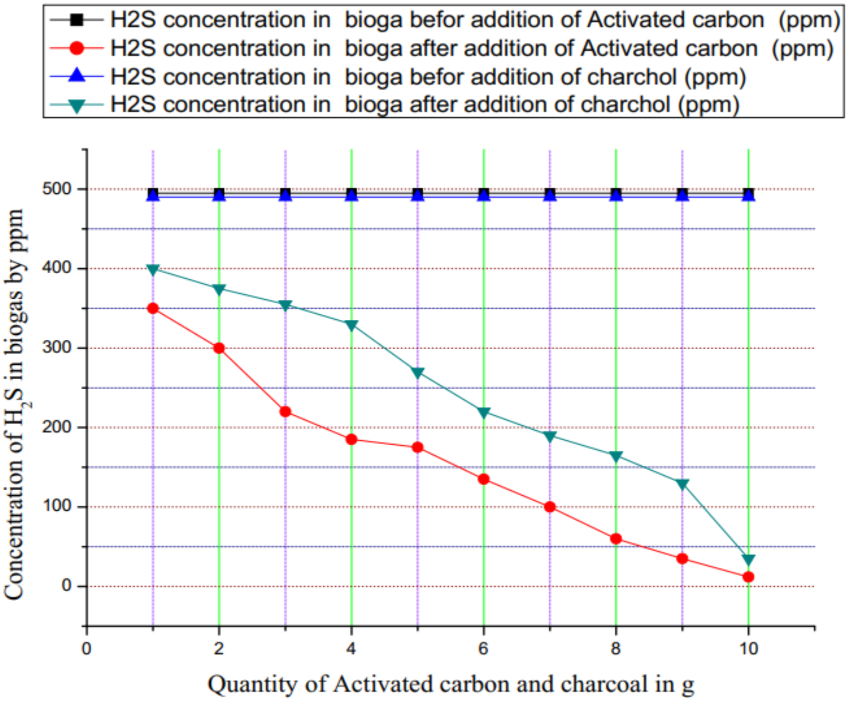


Fig 4.4. Literature result of H_2S removal

4.1.3. Removal of H_2O from untreated biogas

Water vapor is the leading corrosion risk factor when react with H_2S produces deterioration H_2SO_4 acid. It is absorbed and reversibly bound to the surface of drying agents like silica gel and sodium sulfate. The color of the silica gel was changed from blue to pink after absorbing the water vapor from the raw biogas. A steady fall in H_2O-concentration was noticed from 1 to 5 g and 1 to 6 g of silica gel. Although the water, decreasing percentages less from 6 to 10 g than 1 to 5 g. However, the H_2O-concentration decreased after upgrading of the biggest was 5% and

0.89% for treating with 1 and 10 g silica gel. Silica gel is extremely porous and can absorb a large amount of water due to its large internal surface area.

Table 4.5 experimental result

Chemical used	Quantity of chemical used	PH range	Time per experiment	H_2Oconcentration flow before removal	H_2O concentration flow after removal
Silica gel	1-10g	5-8.5	50 min	6.75%	4.25-0.89%

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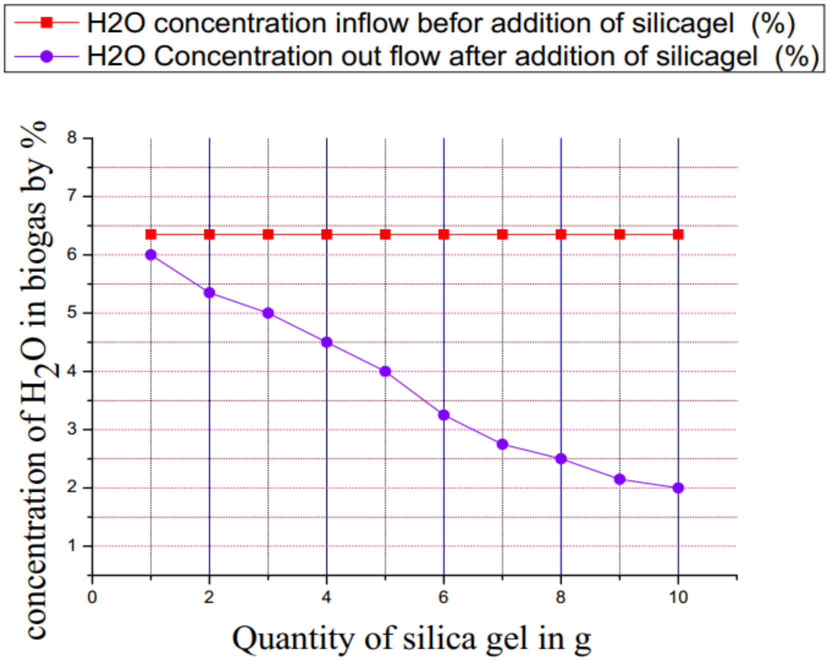

Fig 4.5 Experimental result of water removal

Table 4.6 literature result ((source Muhammad Rashed Al Mamun and Shuichi Tori march 2017)

Chemical used	Quantity of chemical used	PH range	Time per experiment	H_2Oconcentration flow before removal	H_2O concentration flow after removal
Silica gel	1-10g	5-8.5	75 min	6.45%	6-0.95%

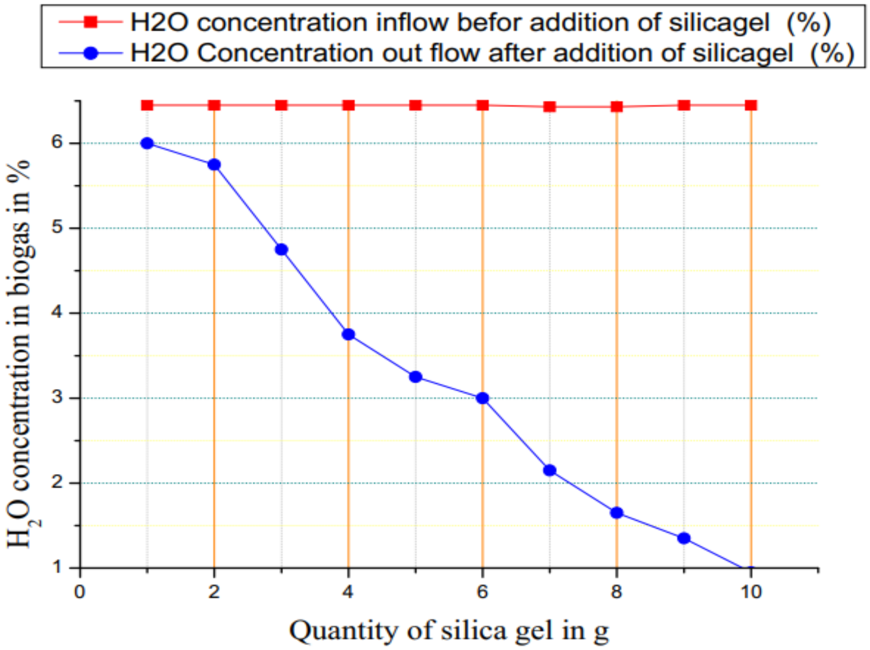

Fig 4.6 Literature result of water removal

4.2. Comparative results study of removal efficiency

the comparative contaminant removal efficiencies with respect to chemical substances. Of all the materials the removal efficiency was increased almost linearly with increases the mass of chemical agents. The removal efficiency was the highest using those chemicals, with efficiency results such as 91.5%,87,96%, 89,90%, for CO_2, H_2S, and H_2O, respectively during the experiments. The corresponding methane enrichment is that 88%.it is observed that the removal efficiency was fluctuated depending on its inflow concentrations. However, the removal efficiency, increased dramatically at 1 g to 9 g, and the increasing tendency is going up depending up on the quantity of the chemical usage.it is concluded that chemical purification process would considered as the best way to upgrade biogas by enhancing the CH_4 concentration. From the results indicated using method-1 which is using NaOH, activated carbon, and Silcagel is good enough when we compare to method- 2 of using KOH and wood charcoal. It also describes that adsorbing efficiencies depend on the degree of saturation of the adsorbent and on the ratio of the gas flow and the mass of adsorbing substance. The removal efficiency was the highest in using method 1, with efficiency results such as 91.5%, 96.6.0%, and 89.99% and in method-2 85%, 88%, and 89%, of CO2, H2S and H2O respectively, with a corresponding CH4 enrichment of 87.5% to 97.2%, can be achieved in comparison to the initial average CH_4-concentration of 64.5%.

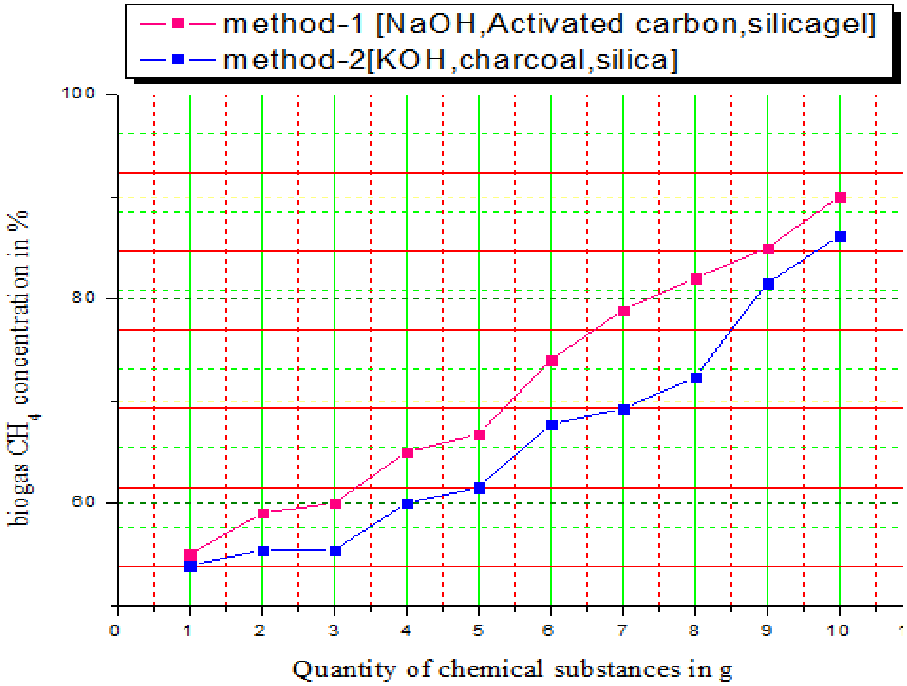

Fig 4.7 Methane enrichment

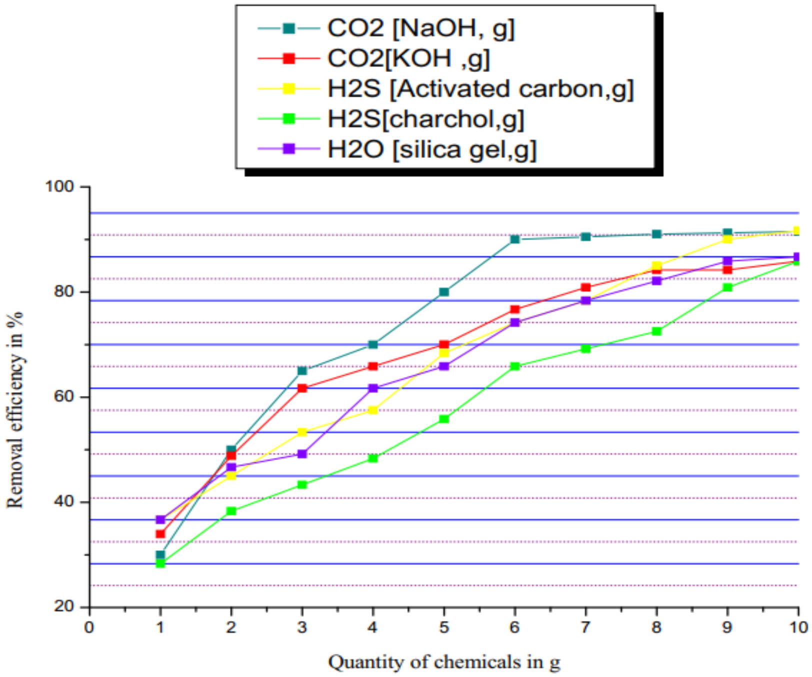

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Fig 4.8 comparation of the general removal efficiency

The absorption of contaminants in a given chemical solutions has been studied as a function of the pH of the solution and the concentration of methane in the scrubber at the start of an experiment, is when the pH was brought to a value of approximately 5 by adding some HCl. At a pH of approximately 5, the methane uptake of the solution decreased slightly and a small amount of NH_3 was added to bring the pH of the solution 0.5 intervals from 5 to 8.5 to improve the uptake of the solution and to visualize the concentration of methane in the solution.

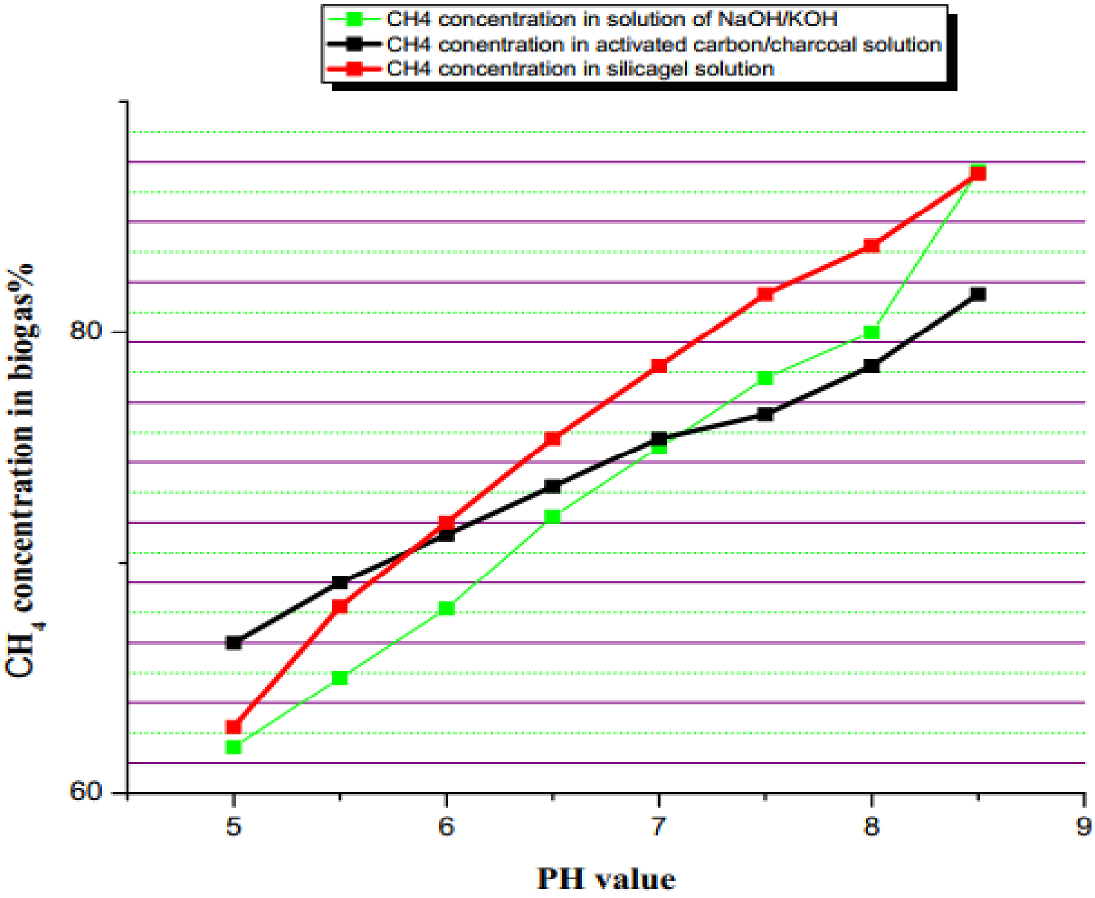

Fig 4.9 Methane concentration under PH solution

Matlab result for biogas production by volume with water model at different temperature and K

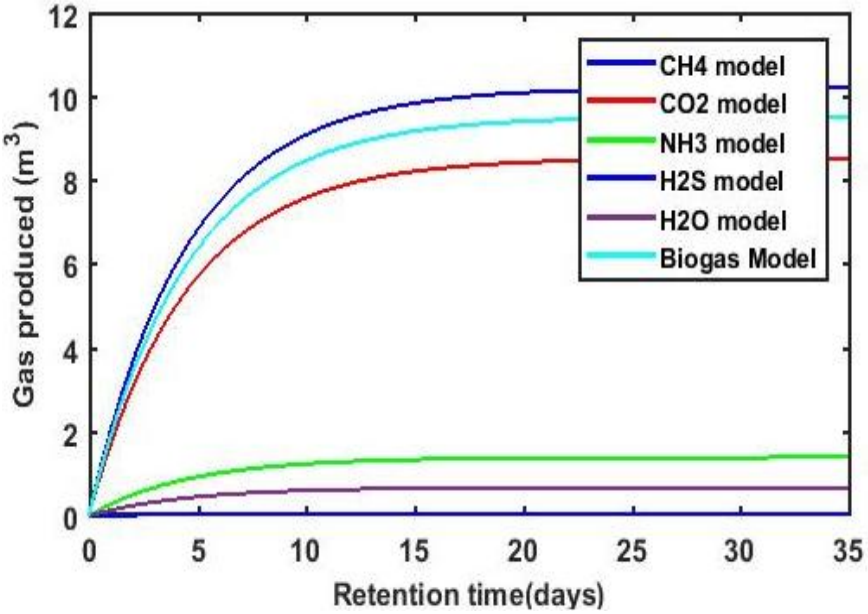

Fig 4.10 Matlab result at T=311k and K=2.7×10^{-6} of biogas production

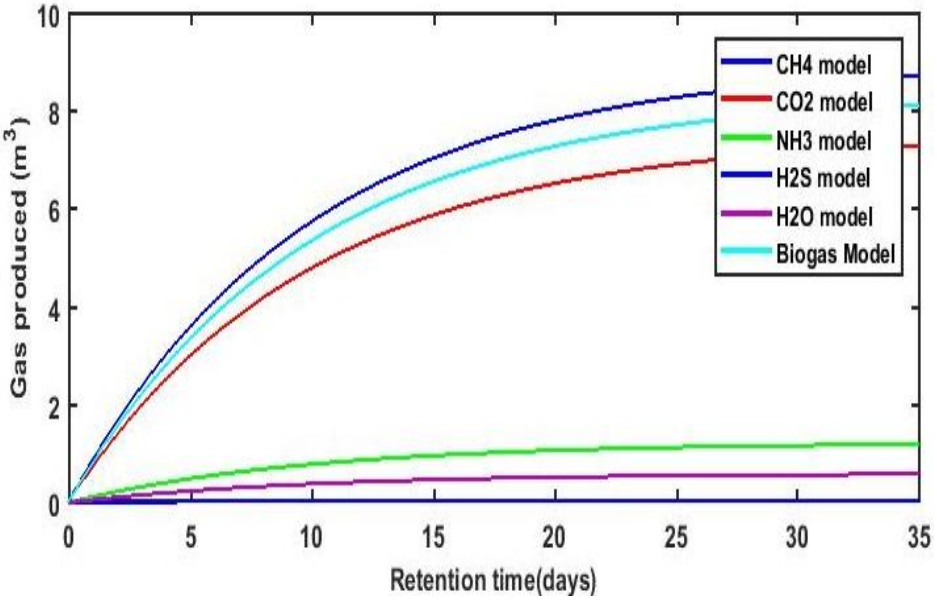

Fig 4.11 Matlab result at T=273k and K=1.25×10^{-6} of biogas production

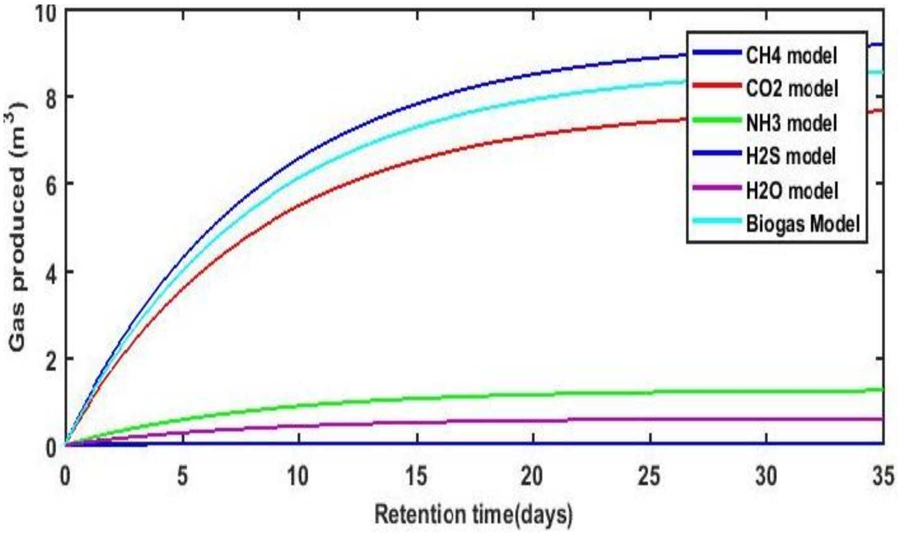

Fig 4.12 Matlab result at T=283k and K=1.5 $\times 10^{-6}$ of biogas production

Matlab result of gas production in (g) and its chemical consumption during purification process from Fig 4.13.for the expected amount of gas production the quantity of chemical needed to remove the contaminant from biogas was determined based on this optimized quantity of chemicals since the code was conducted also to calculate quantity of chemicals needed in the side of gas production.

```
Gasses produced in g

============================================================================

============================================================================

During the process 3881.32 g of CO2 is produced

============================================================================

During the process 2198.53 g of CH4 is produced

----------------------------------------------------------------------------------

During the process 1691.17 g of H2O is produced

---------------------------------------------------------------------------

During the process 21.7979 g of H2S is produced

---------------------------------------------------------------------------

To remove the H2O produced, a minimum of 297.647 g of Silica gel is required
```

```
==========================================================================

To remove the CO2 produced, a minimum of 698.638 g of NaOH is required

==========================================================================

To remove the H2S produced, a minimum of 294.708 g of Activated carbon is required

==========================================================================

To remove the CO2 produced, a minimum of 349.319 g of kOH is required

==========================================================================

To remove the H2S produced, a minimum of 251.29 g of charcoal is required

==========================================================================
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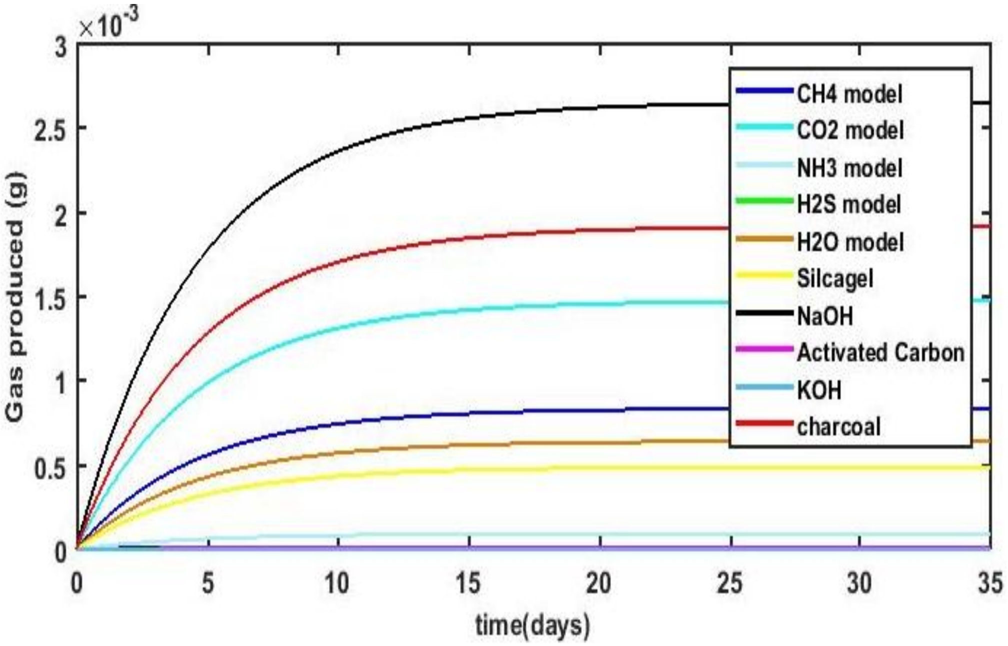

Fig 4.13 Matlab result of chemical model

CHAPTER FIVE

5.1. Compression of Upgraded Gas

In order to reduce the storage requirement, concentration of energy content and to increase pressure to the level needed to overcome resistance to gas flows the upgraded gas must be compressed. Sometimes the production pressure of a biogas source does not match the pressure requirements of the gas utilization equipment. Compression can eliminate the mismatch and assurance for the efficient operation of the equipment. Moreover, large biogas systems rely on compression to reduce the size of the gas storage facility or to transport the biogas to a pipeline. The choice of either a blower or compressor depends on the amount of pressure increase needed (James L. Waish et al., 1988).

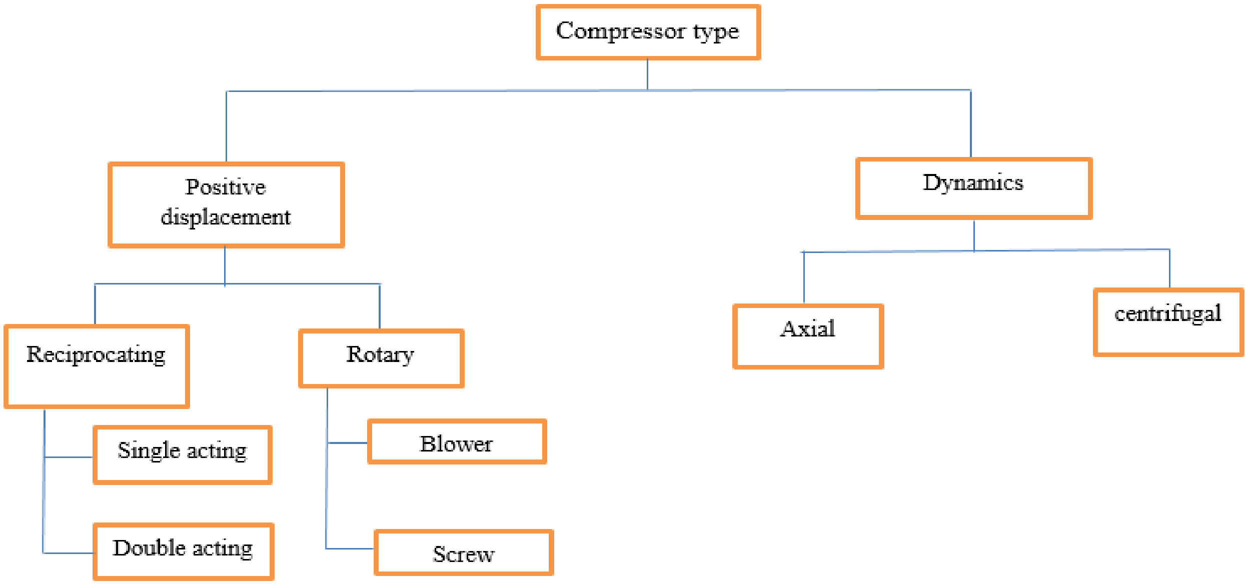

Fig 5.1 classification of compressor

5.2. Parameters Used for The Selection of a Biomethane Compressors

In order to determine what type of compressor system is needed to accomplish the job, a variety of detailed data is needed to be discerned. As a minimum, a precise understanding of the Following data is required:

- Gas being handled
- Flow rate

- Suction and discharge pressure
- Site elevation (or local barometric pressure)
- Suction temperature
- Capacity
- Specific heat ratio of the gas

5.2.1. **Capacity**:

To size a compressor the capacity must be stated as the volume of gas flow at the compressor's suction condition. This volume is normally referred to as inlet cubic meters per hour (Nm^3/hrs.) Compression was carried out through maintaining on an ambient condition since the compression was tried to keep constant the temperature with intermittent compression, and the heat loss was minimized with continuous compression at a given constant temperature. The pressure and volume of the gas at various point of compression can be noted using a pressure gauge and flow meter respectively. For storing gas after compression an LPG cylinder was used.LPG cylinders have a volumetric of 33liters and a net weight 15.4kg.LPG exerts a pressure of 5-7 bars while stored in the cylinder. However, they are designed for a pressure of 25.3bar. [Source: Nepal Standards]

5.2.2. Calculating Compression ratio

Compression ratio (R) is the ratio of discharge pressure to suction pressure

$R = \frac{P_d}{P_s}$ (P_d And P_s must be absolute values)

A single stage compressor has only a single R value. A two-stage compressor has three R values.

R = Total compression ratio for the compressor

$R_1 =$ Compression ratio for the first stage

R_2 = Compression ratio for the second stage

$R = \frac{P_d}{P_s}, R_1 = \frac{P_i}{P_s}, R_2 = \frac{P_d}{P_i}$ ………………………………………………………………….. (5.1)

P_s =suction pressure

P_d=discharge pressure

P_i = inter stage presure : - the pressure between the 1st and 2nd stage of the compressor

5.2.3. Choosing a stage of compressor

The choice of the proper number of compression stages is largely based on the compression ratio. Here are some guidelines for choosing the proper number of stages:

Table 5.1 Compression ratio vs. Proper number of Stages (Source: NPC, 1993)

R value	Number of stages
1-3	Single stage
3-5	Single stage, occasionally two stages
5-7	Two stages, occasionally two stages
7-10	Two stages
10-15	Usually two stages, occasionally three stages
15+	Three stages

In this paper of the compression process part the compressor we are going to use during compression stage must full fill the following criteria's that are selected from catalog for compressing the upgraded gas so for this purpose

The gas being handled is biomethane/upgraded biogas

Flow rate=10 $\frac{m^3}{sec}$, for the compressor selected from catalog

Suction pressure: -The pressure at the compressor inlet expressed, P_s= 1.06bar

Discharge pressure: - The pressure at the compressor discharge expressed, P_d= 10bar

Suction temperature (T_s) = 32℃ (305 K)

Power: -

R=$\frac{P_d}{P_s}$, $P_s = 1.06bar + 0.76\ bar = 1.82bar$

$$P_d = 10bar + 0.76\ bar = 10.76bar$$

$$R = \frac{10.76}{1.82} = 5.912, two\ stage\ compressor\ is\ best\ suited$$

5.2.4. calculate the discharge temperature (T_d)

$$T_d = T_s(\ \frac{P_d}{P_s})^{\frac{n-1}{n}} = T_s R^{\frac{n-1}{n}} \quad \ldots\ldots (5.2)$$

T_s = suction temperature = 32℃ (305K)

P_s =suction pressure = 1.06bar

P_d=discharge pressure = 10bar

R= compression ratio = 5.912

n = specific heat ratio of the gas = 1.3 for biogas

$$\mathrm{T_d} = 305\ (\ \frac{10.76}{1.82})^{\frac{1.3-1}{1.3}} = 459.22\ \mathrm{K}$$

5.2.5. determine the minimum rpm required

With the compressor model and Required Piston Displacement known, the minimum RPM required can be calculated

$$\mathrm{RPM}_{\mathrm{min}} = \frac{100PD_R}{PD_{100}} \quad \ldots\ldots (5.3)$$

$\mathrm{PD_R}$ = Required Piston Displacement

PD_{100}= Piston Displacement per 100 RPM

Table 5.2 compressor stage with their size vs RPM

	Compressor size	PD per 100 RPM (PD_{100})	
	161,162,163	2.05 ft^3	3.48 m^3
	342,343	1.97 ft^3	3.34 m^3

Single stage	361,362,363	4.36 ft^3	7.41 m^3
	642,643	3.84 ft^3	6.52 m^3
	601,602,603	7.78ft^3	13.2m^3
	942	14.99 ft^3	25.5 m^3
Two-stage	172,173	1.02 ft^3	1.73 m^3
	372,373	2.92 ft^3	4.96 m^3
	612,613	6.54 ft^3	11.1 m^3

Compressing biogas requires a gas compressor suitable for flammable gases. These differ from regular compression in several respects (James L. Waish et al., 1988).so from its specification the minimum RPM is 1200rpm.

- The cylinder is located further from the crankcase
- Free of non-ferrous metal
- Condensate control
- Condensate washed out on suction side,
- Passageways are provided to vent leaks away from the crankcase and prevent explosions
- Inlet and exhaust ports are designed to let contaminants pass through instead of collect in the compressor.

5.3. Cylinder Selection Criteria's

LPG cylinder is a type of pressure vessel that needs a high tensile and compressive strength to store pressurized gas. The most common types of material that was used to manufacture LPG cylinder is steel but the steel is heavier and has got some safety problems. In addition to this the steel progressively corrodes. So there arises a need to rectify these problems using some other alternatives in order to select an appropriate material.to overcome these types of problems the least expensive and most versatile of the heat-treatable aluminum alloys (Aluminum 6061 T6 alloy cylinder) is best suited for this purpose It offers a range of good mechanical properties and good corrosion resistance. It can be fabricated by most of the commonly used techniques. In the annealed condition it has good workability. It is welded by all methods and can be furnace brazed with a thin surface layer of high purity aluminum to improve both appearance and corrosion resistance.

5.3.1. Thickness requirement considering internal pressure

Material – Al 6061 T6 alloy

$\sigma_t =$ Yield strength of Aluminum 6061 T6 alloy – 279.99 MPa

$P_i =$internal pressure = 12bar (1.2MPa)

$D_i =$internal diameter = 314.4mm

Thickness required for the cylindrical portion

$$t = \frac{P_i D_i}{2\sigma_t} = \frac{1.2\times 314.4}{2\times 280} = 0.674mm \qquad (5.4)$$

Thickness required for the end dome

$$t = \frac{P_i D_i}{4\sigma_t} = \frac{1.2\times 314.4}{4\times 280} = 0.337mm \qquad (5.5)$$

Taking the greater value for safety purposes i.e. t = 0.674 mm

5.3.2. Thickness requirement considering internal & external pressure

$$t = \frac{D_i}{2}\left[1 - \sqrt{\frac{10FZR_e - \sqrt{3}\times P_h}{10FZR_e}}\right] \text{[ISO 7866]} \qquad (5.6)$$

Where,

P_h=Hydrostatic test pressure in bar above atmospheric pressure 10bar

D_i=Internal diameter of the cylinder 314.4mm

R_e= Yield strength 279.99MPa

R_g= Ultimate strength 310 MPa

Z = stress reduction factor = 1

F is the value lesser among $\frac{1.65}{\frac{R_e}{R_g}}$ and 0.95 so that, $F = \frac{1.65}{\frac{280}{310}} = 1.827$

Therefore, *F* will be the value lesser among 1.827 taking F= 0.95.

$$t=\frac{314.4}{2}\left[1-\sqrt{\frac{10\times0.95\times1\times280-\sqrt{3}\times10}{10\times0.95\times1\times280}}\right]=0.692mm \text{ ………………………………… (5.7)}$$

5.3.3. Stress calculation for Al 6061 T6 alloy cylinder

Young's modulus, E =71 GPa

Thickness of cylinder = 0.692mm

Longitudinal stress

$$\sigma_L=\frac{P_iD_i}{4t}=\frac{1.2mpa\times314.4}{4\times0.692}=136.3Mpa \text{ ………………………………………… (5.8)}$$

Hoop stress

$$\sigma_L=\frac{P_iD_i}{2t}=\frac{1.2mpa\times314.4}{2\times.692}=272.6\ Mpa \text{ ……………………………………….. (5.9)}$$

Von-mises stress

$$\sigma_v=\sqrt{\sigma_1^2+\sigma_2^2-\sigma_1\sigma_2} \text{ …………………………………................................ (5.10)}$$

$$=\sqrt{136.3^2+272.6^2-(136.3\times272.6)}=851.45N/mm^2$$

Longitudinal Deformation

$$\delta=\frac{Pr^2(1-\vartheta)}{2Et} \text{ …………………………….. (5.11)}$$

$$=\frac{1.2\times(\frac{314.4}{2})^2\times(1-0.33)}{2\times0.692\times71\times10^3}=0.20219mm$$

5.3.4. Calculation of volume of Al 6061 T6 cylinder

Volume of cylindrical portion

$$V_{cyl}=\pi h(r_0^2-r_i^2) \text{ ……………………………………………………………… (5.12)}$$

$$V_{cyl}=\pi\times368\times[(\frac{322+2\times0.692}{2})^2-(\frac{314.4+2\times0.692}{2})^2 =1{,}402{,}507.7685\ mm^3$$

Volume of spherical portion,

$$V_{sp} = \frac{4}{3} \times \pi \times (r_0^3 - r_i^3) \text{ ……………………………………………………… (5.13)}$$

$$= \frac{4}{3} \times \pi \times [(\frac{322}{2})^3 - (\frac{314.4}{2})^3] = 2{,}739{,}605.9\ mm^3$$

Total volume of the aluminum 6061 T6 LPG cylinder

$$1{,}402{,}102.87 + 2{,}739605.9 = 4{,}142{,}113.67 \times 10^{-9}\ mm^3 = .0414\ m^3$$

Calculation of mass of Al 6061 T6 cylinder

Mass of aluminum alloy LPG cylinder = density of the cylinder × volume of the cylinder

Density of Al6061 T6 cylinder = 2770 Kg/m^3

Volume of Al6061 T6 cylinder = $4{,}142{,}113.67 \times 10^{-9}\ mm^3$

mass of aluminum 6061 T6 cylinder = $2680 \times 2119674.37 \times 10^{-9}$ = 5.87 Kg

The weight of Al 6061 T6 cylinder without considering the foot ring, VP ring, valve, bung, foot ring and coatings =5.87 kg

5.4. Power Needed for Compression

The energy required for compression represents a major operating cost of a biogas system. Accordingly, estimating the energy requirement becomes an important component of the system design effort. Estimates are usually based on adiabatic compression process (compression without cooling) since such a calculation estimates the minimum energy required for compression in a frictionless compressor (James L. Waish et al., 1998).

Mathematically, the relationship between the system pressures, the compressor capacity, and the energy required for compression in a frictionless, adiabatic compressor can be stated as: -

$$w = c_1 R T_1 [(\frac{p_2}{p_1})^{c_2} - 1] \text{ …………………………………………………………… (5.14)}$$

K = Ratio of specific heats of the biogas $\frac{C_p}{C_v}$ = 1.3

R = Gas constant for the biogas = 8.314J/mol K

Biogas production rate = 0.425

$$C_1 = \frac{K}{k-1} = 4.33,\ \ C_2 = \frac{k-1}{k} = 0.231$$

T_1 = Initial temperature (K) =305k = 32℃

p_1 = Initial pressure (kPa) = 1.06bar

p_2 = Final pressure (kPa) = 10bar

$$W = C_1 R T_1 \left[\left(\frac{p_2}{p_1}\right)^{C_2} - 1\right]$$

$$w = 4.33 \times 8.314 \times 305 \left[\left(\frac{10}{1.06}^{0.23}\right) - 1\right] = 7586.403 watt = 7.586 kw$$

The value of "W " represents the amount of energy required to compress biogas of a known composition adiabatically**.** However, compressors are never 100% efficient because of friction and heat transfer that occur during the compression process and therefore the actual energy required will be greater than computed using the preceding equation. It should be noted that manufacturers' literature will indicate different efficiencies for almost every compressor. Confusion can be avoided by asking the manufacturer of the compressor being analyzed for the actual energy consumption of the equipment.

5.5. Storage volume for compression process

For adiabatic compression, with no heat transfer across the system boundary (Q = 0), the thermodynamic relation is given by (W.Z. Black & J.G. Hartley, 1995). As biogas is compressed to higher pressures, its mass is pushed into smaller volume. This raises the energy density of the gas and reduces the required storage volume.

$p_1 v_1^k = p_2 v_2^k$ ………………………………………………………………………… (5.15)

Where, k = Adiabatic ratio, $\frac{C_p}{C_v} =$ 1.3 for biogas

$P_1 = 1.06$ bar

$$V_{gas} = V_{init\ tank} - V_{waste} - V_{water} = V_{init\ tank} - \frac{mass\ of\ waste}{density\ of\ waste} - \frac{mass\ of\ water}{density\ of\ water}$$

$$=10{,}000\text{L} - \frac{230kg}{\frac{1200kg}{l}} - \frac{1380kg}{\frac{1000kg}{l}} = 9998.41L = 9.9m^3 \sim 10m^3$$

V_1 = Initial volume of biogas that the plant produces per day = 10m^3/day

P_2 = Compressed raw biogas pressure (10bar) selected from catalogue

V_2 = volume of gas to be Compressed?

$$\mathbf{v_2}^{\mathbf{k}} = \frac{\mathrm{p}_\mathbf{1}\mathbf{v_1}^{\mathbf{k}}}{\mathrm{p}_\mathbf{2}}$$

$$\boldsymbol{V_2} = \left[\frac{\mathrm{p}_\mathbf{1} \times \mathbf{v_1}^{\mathrm{k}}}{\mathrm{p}_\mathbf{2}}\right]^{\frac{1}{\mathrm{k}}}$$

$$=\left[\frac{1.06 \times 10^{1.3}}{10}\right]^{.77} = 2.7\text{m}^3/\text{day}$$

Total biogas compressed per year is = 2.7m^3/day ×290day/year = 782.8m^3/year

CHAPTER SIX

6.1. Financial and Economic Analysis of Biogas Upgrading

Biogas is a renewable energy which is eco-friendly and minimizes expenditure on the foreign exchanges on the import of fossil fuels. The main reason that biogas upgrading plant is not yet applicable in our country is due to lack of technical knowledge, awareness and high availability of resources such as firewood, Charcoal, Kerosene, Electricity and etc. Even though they are expensive. The biogas plant demands a relatively high capital investment. The economics of various different alternatives available for the households need to be analyzed, so that the best one can be chosen.

Any decision for or against the construction and operation of a biogas upgrading plant depends on various technical criteria as well as on a number of economic and utility factors. Users want to know what the plant will offer in the way of profits (cost benefit analysis) and advantages like reduced work load, more reliable energy supplies or improved health

6.2. Determining Biogas demand

There are many ways to approach economic analysis, and the biogas upgrading plant demand depending on the point of view from which plant is considered. The simplest approach is, look at the cash flow position of the plants (GTZ, 1989)

a) **Determining biogas demand on the basis of present consumption**: This involves measuring the present rate of energy consumption in the form of Fire Wood, Charcoal, Kerosene, Electricity etc.

b) **Calculating biogas demand by means of comparable use data**: such data may consist of: -

- Empirical values from neighboring systems, for example biogas consumption per person & day.
- Reference data taken from literature, although this approach involves considerable uncertainty, since cooking energy consumption depends on local culture eating habits; therefore, differ substantially from case to case.

c) **Estimating biogas demand by way of appliance consumption data and assumed periods of use**: - This approach can only work to the extent that the appliances to be used are known in advance.

6.3. Equivalence of Biogas Demand

The equivalent demand of biogas can be determined using the following factors for the fuel to be substitute

1kg of fire wood $\cong 0.2m^3$ biogas

1kg of charcoal $\cong 0.5\ m^3$ biogas

0.6 litter of kerosene $\cong 1m^3$ biogas $(\text{Source: GTZ, } 1989)$

Table 6.1 Some biogas equivalents (Kristofferson & Bokalders, 1991)

application	**1m^3 biogas plant**
lighting	Equal to 60 – 100-watt bulb for 6 hours
cooking	Can cook 3 meals for a family of 5 – 6
fuel	0.7 kg of petrol
electricity	Can generate 1.25kwhr of electricity

Hence, the biogas to be produced from 10m^3 digester can produce 6kw electricity for the cooking energy requirement or for heating and lightening households per day. This indicates that the substrate collected from the cafeterias can serve for the cooking energy requirements or for lighting.

6.3.1. Determining biogas demand on the basis of present energy consumption

Table 6.2 Present energy consumption (Source: by Bekele Gaddisa field survey, 2014)

Source of energy	Monthly fuel consumption per family	
	Unit	Price averagely in birr
Fire wood	(30-50) kg	50
Charcoal	(40-80) kg	120
kerosene	(8-10) kg	135
electricity	~	80
Total =birr 385		

Table 6.3 Requirements and Costs for the upgrading process based on current basis

No	Required material	Description	Qty	Price/cost in birr	
				Unit price	Total price
1	Ball valves	$\emptyset = \frac{1}{2} in$	4	120	480
2	PVC hose pipe	$\emptyset = 8\ in$	7m	50	350
3	Galvanized steel pipe	$\emptyset = \frac{1}{2} in$	135cm	135	155
4	Galvanized socket	$\emptyset = \frac{1}{2} in$	4	45	180
5	raccordion	$\emptyset = 1\ in$	3	230	690
6	Gate valve	$\emptyset = 1\ in$	2	140	280
7	Galvanized Tapes	$\emptyset = \frac{1}{2}\ in$	4	40	160
8	Galvanized tee	$\emptyset = \frac{1}{2} in$	3	45	135
9	NaOH		500gm	850	850
10	KOH		500gm	500	500
11	Activated carbon		500gm	500	500
12	Silica gel		500gm	500	500
13	Compressor		1	15,000	15,000
14	Pump		1	3500	3500
15	Support bars that carry the scrubber	∅ =85mm	3	50	150
16	Labour (fitting installation and support bar welding and electrical works)		3 persons 7 days	214.285	4500
	maintenance cost				4000
	Operating cost				2000
	Total (birr)				22,930
	Contingency (5%)				1146.5
	Total money in birr				24,076.5

6.4. Financial Analysis

Projects are assumed to be economically feasible if the Net Present Value (NPV) is positive, the internal rate of return (IRR) is≥ 20% and a payback period of ≤ 7years.The major parameters that need to be considered for the financial feasibility, of biogas upgrading plants are:

6.4.1. Project life

A biogas upgrading plant could last for more than 20 years depending on the quality of construction and the materials used. However, the economic life of a plant is taken as 10 years mainly because any cost or benefit accrued after 10 years will have insignificant value when discounted to the present worth.

6.4.2. Benefits and Cost

All benefits of a biogas production and upgrading plant cannot be readily priced or even compared with the price of similar products or services in the market. For example, it is difficult to put a money value for the benefit of decrease environmental population. This indicates that even if the financial analysis shows zero net benefit of constructing a biogas plant, it should be interpreted as having positive net benefits owing to the unpriced factors.

The biogas plants produce both biogas and organic fertilizer. The biogas could be used mainly instead of firewood, charcoal, kerosene and etc. while organic fertilizer used to improve crops yield, and so could be used instead of manufactured fertilizers. Therefore; the annual direct financial benefits for biogas plants could be estimated as follows:

6.5. Time Value of Money and Discount Ratio

- Real value of money changes over time. The reasons for such changes are:
- Money of today can be invested to earn a return in the future; and
- People have time preference, i.e. they prefer now to the future

The upgraded biogas can be sold at a price of 3.19 \$/1000ft^3 or 11 \$cent/m^3 or 3.04 birr/ m^3(Norz, 2017). Multiplying this by the total working hours per year gives the total income through the sale of biogas per year.

annual save from selling upgraded biogas is calculated as: -

income biogas [birr/yr.] = upgraded biogas in m^3 throughout the year × Price [birr/m^3] × working hours in yr.

$$= 782.8\ \text{m}^3 \times 3.04\ \text{birr} \times 10\text{hrs} = 23{,}797.016\ \text{birr/year}$$

6.5.1. Net Present Value

As the costs and benefits of a project are spread over the useful years of project life, they need to be expressed in terms of one common denominator to make the comparison possible. Once the annual cash flow of a project is derived, it needs to be discounted so that all values could be compared to the value of a single year. This discounted net cash flow provides a widely used criterion for measuring the profitability of a project. For this purpose, all future values are discounted to make them equivalent to the present value and is expressed as Net Present Value (NPV). The NPV technique measures the worthiness of a project by converting the annual cash flow to a single present value. A positive NPV indicates that the benefits are higher than the costs that accrue over the project life. The process of relating future amount to the present value is known as discounting and is expressed by the following equation:

$$p = \frac{F}{(1+r)^n} \qquad (6.1)$$

Where, P = present sum of money

F = Future sum of money

r = Rate of interest

n = Number of years

The commonly used discount rate is the rate of interest that a bank charges on loans and the opportunity cost of capital in situations where private capital is being committed. The NPV is calculated in

$$P = A\left[\frac{((1+r^n)-1)}{r(r+1^n)}\right] \qquad (6.2)$$

Where, A = annual worth (value)

6.5.2. Benefit Cost Ratio

Benefit-cost ratio (BCR) is another tool for assessing the profitability of a project. If the ratio is greater than unity (i.e. B/C > 1.0) the project is profitably.

6.5.3. Simple Payback Period

Simple payback period is time period required to recover the original investigated for the construction of a plant. It represents the number of years in which the investment is expected to pay for itself. It is given by:

$$SPP = \frac{I_c}{A_s} \quad \text{(6.3)}$$

Where, SPP = Simple payback period

I_C =Initial cost

A_S = Annual saving (benefits)

The net present value, benefit cost ratio and simple payback period are given as follows. The present costs during the lifetime of the project are determined as

$$p_c = I_c + A(\frac{P}{A}, r, n) \quad \text{(6.4)}$$

I$_c$ = Initial cost
A = Annual cost
r = Discount rate assuming (12%)

$$p_c = I_c + A(\frac{P}{A}, r, n)$$

$$24{,}076 + 6000\left[\frac{(1+0.12)^{10}-1}{0.12(0.12+1)^{10}}\right] \text{ at r = 10\%}$$

=57,977 birr

The present value of benefits or saving during the life time of the project

$$P_b = A\left[\frac{(1+r)^n - 1)}{r(1+r)^n}\right] \quad \text{(6.5)}$$

A = Annual benefits

P_b = Total benefits during the lifetime of the project

$$P_b = A\left[\frac{((1+r^n)-1)}{r(r+1^n)}\right] = 23{,}797.016\left[\frac{(1+.12)^{10}-1)}{0.12(1+0.12)^{10}}\right] = 134{,}712.106 \text{ birr}$$

The annual saving is: - $A_s = A_b - A_c$ = 23,797.016 – 6000 = 17,797.016 birr

The Net Present Value is determined as

NPV= $P_b - P_c$ = 134,712.106 – 57,977 = 76,735.016 birr

The simple payback period is

$$\text{SPP} = \frac{\text{I}_\text{c}}{\text{A}_\text{s}} = \frac{24{,}076}{17{,}797.016} = 1.35$$

this means by selling a purified gas from small scale plant it will get back the capital of constructing biogas plant with in a time of less than two years.

The benefit cost ratio

BCR= $\frac{P_b}{P_c} = \frac{134{,}712.106}{57{,}977} = 2.32 \geq 1$ so the project is profitable.

6.6. Main Findings

The goal of this paper (study) was to demonstrate basically simulation and biogas upgrading process experimentally. The analysis of the simulation part was conducted using MATLAB 2017 program and divided in two subsystems the 1st mathematical modeling is biogas production and the second one is mathematical development of biogas purification based on selected chemicals from related literatures.

The first system has the same design procedure and mathematical developing system for all the difference biogas production technologies. The second system of the purification process was developed from the biogas production system model. Based on this analysis's the corresponding graphical results of production process and upgrading one was conducted depending on the amount of waste, reaction rate, retention time and amount of chemical used for purification. The experimental result shows a combined upgrading chemical method could offer a viable alternative for methane enrichment in biogas, since all contaminants capture occurs in the same process. The results showed that the CH_4-concentration is improved by reducing the CO_2, H_2S and H_2O content of the biogas to a considerably lower concentration and the MATLAB result shows the amount of chemical substances in g to be involved in the purification process and the impurities with the variation of time.

Compressing biogas reduces storage requirements, concentrates energy content and increases pressure to the level needed to overcome resistance to gas flow. Accordingly, by applying biogas compressor for the system, that 2.7m^3/day volume of biogas is stored in 4.142 m^3 of pressure vessel. Also, compressor increases pressure from 1.82 bar to 10.76 bar to overcome the problem of mismatch of pressure requirements of gas utilization equipment.

Financial study has shown that The NPV was calculated assuming an economic running time of the plant 10 years for the biogas upgrading plant, at a discount rate of 10%. So that the net present value of the small-scale plant is Birr 76,735.018 which is positive. if the gas was used as an energy demand its benefit cost ratio is 2.32 which is greater than one and the simple payback period is 1 years and 3monthes. so this all results indicating that the project is profitable

CHAPTER SEVEN

CONCLUSION AND RECOMMENDATION

7.1. Conclusion

The source of material used in biogas production has a significant effect on the composition of biogas and its purification process. There are various methods of biogas purification available, all of them are not quite acceptable in the rural areas. Most of them are costly and are difficult to handle There are various methods of biogas purification available, all of them are not quite acceptable in the rural areas. Most of them are costly and are difficult to handle. Among them the chemical absorption is found to the easiest one but due to the use of aqueous solution of chemicals, this method is found to be difficult to handle. That is why the chemical biogas purification process with dry chemical was used or prepared as Combined chemical upgrading method that could offer a viable alternative for methane enrichment in biogas, since all contaminants capture occurs in the same process. The results showed that the CH_4-concentration is improved by reducing the CO_2, H_2S and H_2O content of the biogas to a considerably lower concentration with the removal of chemical substances. as carbon dioxide absorber, H_2S and water removal is used in the present study using NaOH, KOH, activated carbon, Charcoal and silica gel as the chemical absorbers. The removal efficiency was the highest in method 1 than in method 2, with efficiency results such as 91.5%, 95.0%, and 97.1% and 85.3%, 91.8%, and 81.5%, of CO_2, H_2S and H_2O respectively, with a corresponding average CH_4 enrichment of 85.5% and 87.2%, can be achieved in comparison to the initial average CH_4-concentration of 64.5%.the simulation result for the upgrading process also conducted through Matlab and validated with the experimental one based on the objective finally it was 90% approximately equal.

Compressing biogas reduces storage requirements, concentrates energy content and increases pressure to the level needed to overcome resistance to gas flow. Accordingly, by applying biogas compressor for the system, the 2.7m^3 volume biogas is stored in 4.252m^3 of LPG cylinder. Also compressor increases pressure from 1.82 bar to 10.76 bars to overcome the problem of mismatch of pressure requirements of gas utilization equipment.

Financial study has shown that net present value of the plant is Birr 76,735.018 which is positive if the plant uses for all different types of energy demand and benefit cost ratio is 2.32 which is greater than one and the simple payback period is 1.32 years.

7.2. Recommendation and Future work

This project has considered the development of an experimental work and Matlab model to simulate a biogas upgrading process. A Matlab model has been developed to simulate concentration of impurities removed from a produced volume of methane gas in order to get the expected methane purity in an upgrading process, using base case parameters from a food waste biogas production processes.

Since the Matlab code took a long time to start running correctly, there was not enough time to run simulations of the Laboratory scrubber model. For future work and purposes, the Laboratory scrubber can be simulated with the Matlab code, as a further development.

Also, individually the absorption, adsorption and desorption process math's model has not been considered in this project work. The absorption, adsorption and desorption code building process can further be developed in the future taking the Laboratory biogas production process having as a base case. Sensitivity analysis also taken as a future work.

Since some specific materials like a compressor and cylinder was not found in the market based on the design specification, volume and mass which will be calculated in the paper the practical compression work was not conducted but the design and selection process was completed.

This study recommends that industrial scale plants throughout a detail research on biogas upgrading and its economic feasibility for the removal of biogas contaminants be built alongside biogas digesters to ensure the safety of the environment and wellbeing of the consumers.

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APPENDIXES

Appendix – 1: - Compressor Specification

Technical data of a compressor needed for compression (GA 7.5 – 250 Source: [China Mainland Air-Compressors. http://www.atlascopco.com]

Model 50HZ	Capacity (m^3/min)				Motor power		Dimension (mm)			weight	Noise level	Outlet diameter
	7bar	8bar	10bar	12bar	KW	HP	L	W	H	Kg	dB(A)	
GA7.5	1.38	1.31	1.11	0.95	7.5	10	1000	640	1000	500	62±2	G3/4”
GA11	1.91	1.81	1.52	1.35	11	15	1000	640	1000	540	62±2	G3/4”
GA15	2.68	2.45	2.21	1.73	15	20	1300	780	1200	710	63±2	G1”
GA18.5	3.26	3.13	2.71	2.21	18.5	25	1300	780	1200	800	65±2	G1”
GA22	3.77	3.62	3.23	2.72	22	30	1300	780	1200	820	65±2	G1”
GA30	5.2	4.92	4.22	3.81	30	40	1600	930	1350	980	66±2	G1 ½”
GA37	6.58	6.26	5.8	5.06	37	50	1715	1090	1635	1120	63±2	G1 ½”
GA45	8.3	7.5	6.3	5.84	45	60	1765	1110	1475	1260	65±2	G1 ½”
GA55	10.8	10.1	8.5	7.69	55	75	2045	1250	1705	1750	65±2	G2”
GA75	13.5	12.7	11.3	10	75	100	2045	1250	1705	1820	68±2	G2”
GA90	16.2	15.2	14.3	12.9	90	120	2329	1516	1745	2200	68±2	DN65
GA110	21.6	20.1	17.5	16	110	150	2578	1656	1920	2950	68±2	DN65
GA132	25.2	24	21	18.3	132	175	2578	1656	1920	3550	72±2	DN65
GA160	28.7	27.6	25.3	22.4	160	200	2856	1898	1895	3880	72±2	DN80
GA185	32.5	30.8	28.2	25.1	185	250	2856	1898	1895	4050	72±2	DN80
GA220	36.8	34.7	30.8	28.9	220	300	3092	1944	2143	4700	76±2	DN80
GA250	42.7	40.8	40.8	34	250	350	3092	1944	2143	5100	76±2	DN80

compressor stage with their size vs RPM (source Blackmer American compressor selection and sizing)

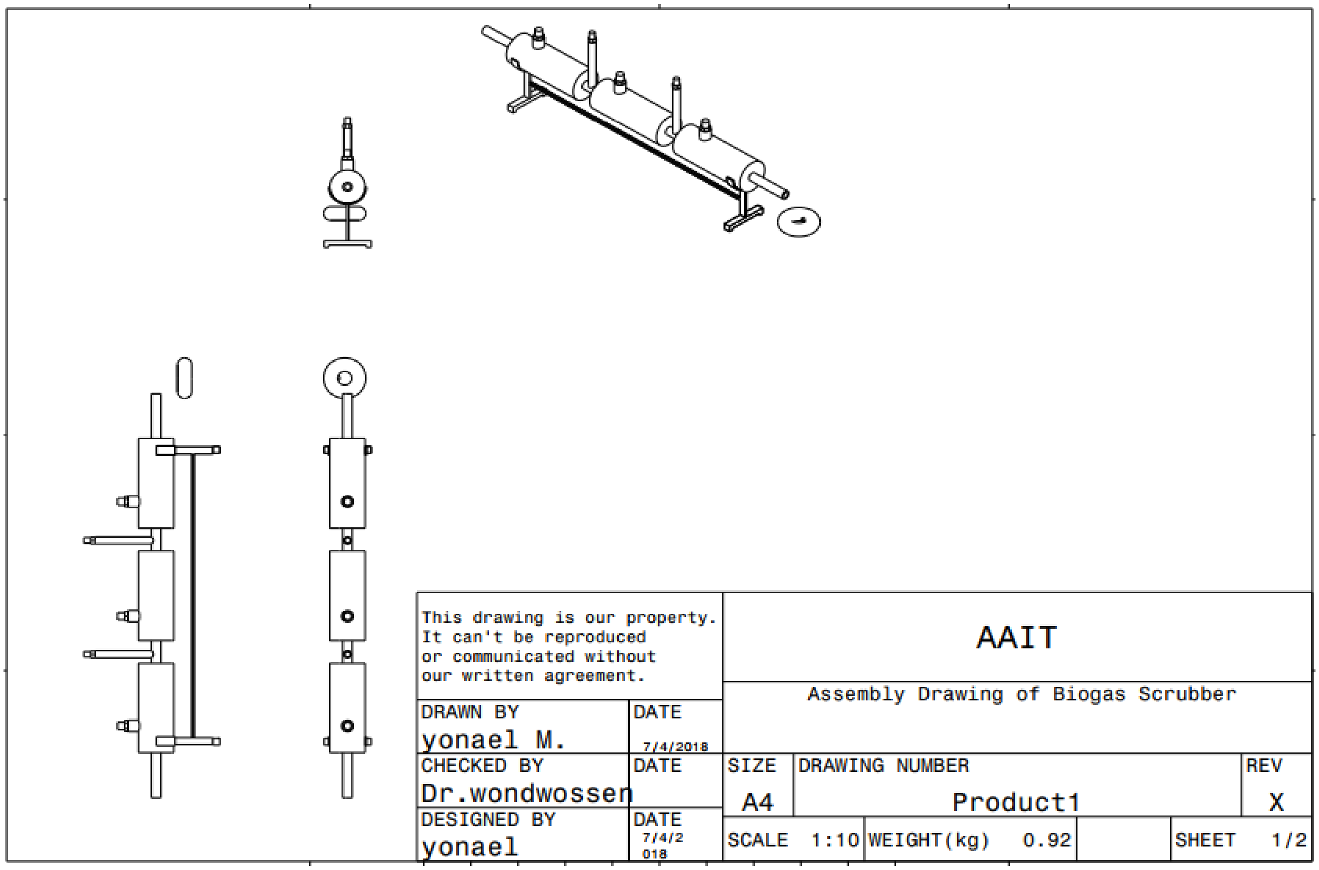
	Compressor size	PD per 100 RPM (PD_{100})	
Single stage	161,162,163	2.05 ft^3	3.48 m^3
	342,343	1.97 ft^3	3.34 m^3
	361,362,363	4.36 ft^3	7.41 m^3
	642,643	3.84 ft^3	6.52 m^3
	601,602,603	7.78ft^3	13.2m^3
	942	14.99 ft^3	25.5 m^3
Two-stage	172,173	1.02 ft^3	1.73 m^3
	372,373	2.92 ft^3	4.96 m^3
	612,613	6.54 ft^3	11.1 m^3

Properties of Welded Mild Steel, Al6061-T6 and Alumina (source Faculty of Computer and Mathematical Sciences, University Technology MARA Sarawak 2012)

Material	Temperature (℃)	Thermal conductivity (W.m^{-1}. K^{-1})	Heat capacity (J. Kg^{-1}. K^{-1})	Density (Kg.m^{-3})	Thermal expansion (×10^{-6}K^{-1})	Young’s modulus (GPa)	Yield stress (MPa)	Poisson’s ratio	Melting point (℃)
Aluminum alloy 6061-T6	0	162	917	2703	22.4	70	279	0.33	582 - 652
	98	177	978	2685	24.61	66.2	264.6		
	201	192	1028	2657	24.6	59.2	218.6		
	316	207	1078	2630	27.6	47.78	66.2		
	428	223	1133	2602	29.6	31.72	17.9		
	571	253	1230	2574	34.2	0	0		
Alumina	25 - 727	16.7	950	3950	7.5	300	-	0.2	2127
	0	34.5	470						
	98	345	485						
	201	33.8	520						

Steel	316	31	560	7800	10.1 –16.6	68.9-207	-	0.23-0.3	1230 - 1530
	428	28.5	620						
	571	26.8	700						
	650	25.8	760						

Appendix -2: - Assembly drawing



Appendix – 3: - Matlab Code for Biogas Production Model

```
%MATLAB SIMULATION FOR 230 Kg/day INPUT
% This code helps to size and give dimensions to Biogas plant
%% Sizing of Biogas
prompt = 'Insert Daily input in Kg? ';
Dailyinput = input(prompt);
prompt = 'Insert Retention Time_No of days? ';
RT = input(prompt);
prompt = 'Insert Concentration_of_TS? ';
Concentration_of_TS = input(prompt);
TS=(Dailyinput)*0.3033;
water_required = (TS/Concentration_of_TS)-(Dailyinput);
Total_influent_required = (TS/Concentration_of_TS);
TS=(Dailyinput)*0.3033;
Vgs= 0.5*TS*Dailyinput*0.158;
```

```
Vh=Vgs;
%% Kinetic Model
% kinetic coefficient
k = 2.7*10^-6;
% mass flow rate in (kg/day)
dAdtin = 0;
% mass flow rate out
dAdtout = 0;
% these are molar masses of each element
mm_carbon = 12.0107;
mm_hydrogen = 1.0079;
mm_oxygen = 15.999;
mm_nitrogen = 14.0067;
mm_sulphur = 32.065;
% For C_n H_a O_b N_c S_d + H20 => CO2 + CH4 + H2S+ NH3 + H2O
% These constants come from the ultimate analysis
% These constants dictate the coefficients of each term
nbymass = 0.45405;
abymass = 0.07655;
bbymass = 0.42915;
cbymass = 0.03945;
dbymass = 0.004;
% to get molar ratios we divide by molar mass
n = nbymass/mm_carbon;
a = abymass/mm_hydrogen;
b = bbymass/mm_oxygen;
c= cbymass/mm_nitrogen;
d= dbymass/mm_sulphur;
% These are the coefficients in front of each component of the reaction.
% C_n H_a O_b N_c S_d + c_1* H20 --> c_2*CO2 + c_3*CH4+c_4*NH3 + c_5*H2S +
% c_6*H2O
c_1 = n - a/4 -b/2+(3/4) *c+d/2;
c_2 = n/2 -a/8 + b/4+(3/8) *c+d/4;
c_3 = n/2 + a/8 - b/4-(3/8) *c-d/4;
c_4 = c;
c_5 = d;
%c_6 is 7.5% by mass of the methane gas
c_6 = (0.075*c_3*(mm_carbon + 4*mm_hydrogen))/ (2*mm_hydrogen + mm_oxygen);

% These are the molar masses of each component
mm_A = mm_carbon*n + mm_hydrogen*a + mm_oxygen*b+ mm_nitrogen*c+
mm_sulphur*d;
mm_B = 2*mm_hydrogen + mm_oxygen;
mm_C = mm_carbon + 2*mm_oxygen;
mm_D = mm_carbon + 4*mm_hydrogen;
mm_E = mm_nitrogen + 3*mm_hydrogen;
mm_F = 2*mm_hydrogen mm_sulphur;
mm_G = 2*mm_hydrogen + mm_oxygen;
% These are the masses of each component per mol of food waste
m_A = mm_A;
m_B = c_1*mm_B;
m_C = c_2*mm_C;
m_D = c_3*mm_D;
m_E = c_4*mm_E;
m_F = c_5*mm_F;
m_G = c_6*mm_G;
```

```
ratio = m_C/ (m_C + m_D + m_E + m_F + m_G);
% Initial conditions, mass in Kg, digester capacity in m3, volume of reaction
in m3
mass_of_FoodWaste = Dailyinput;
mass_of_water = water_required;
density_of_FoodWaste = 1120;
density_of_water = 1000;
volume_of_reaction = (mass_of_FoodWaste/density_of_FoodWaste +
mass_of_water/density_of_water);
digester_capacity=(Total_influent_required*RT)/ (0.8);
Ahat_0 = mass_of_FoodWaste/mm_A/digester_capacity;
Bhat_0 = mass_of_water/mm_B/digester_capacity;
Chat_0 = 0;
Dhat_0 = 0;
Ehat_0 = 0;
Fhat_0 = 0;
Ghat_0 = 0;
dAhatdt_0 = -k*Ahat_0*(Bhat_0^(c_1));
dBhatdt_0 = -k*Ahat_0*(Bhat_0^(c_1)) *c_1;
dChatdt_0 = k*Ahat_0*(Bhat_0^(c_1)) *c_2;
dDhatdt_0 = k*Ahat_0*(Bhat_0^(c_1)) *c_3;
dEhatdt_0 = k*Ahat_0*(Bhat_0^(c_1)) *c_4;
dFhatdt_0 = k*Ahat_0*(Bhat_0^(c_1)) *c_5;
dGhatdt_0 = k*Ahat_0*(Bhat_0^(c_1)) *c_6;
%% Can iterate this process for very small steps of time to approximate the
% new concentration of each component of the reaction
% Concentration of each component put into a row vector
tfinal = RT*24*60*60; % retention time: RT
t = (1: tfinal);
Ahat = zeros (1, tfinal);
Bhat = zeros (1, tfinal);
Chat = zeros (1, tfinal);
Dhat = zeros (1, tfinal);
Ehat = zeros (1, tfinal);
Fhat = zeros (1, tfinal);
Ghat = zeros (1, tfinal);
% Rate of concentration of each component put into a row vector
dAhatdt = zeros (1, tfinal);
dBhatdt = zeros (1, tfinal);
dChatdt = zeros (1, tfinal);
dDhatdt = zeros (1, tfinal);
dEhatdt = zeros (1, tfinal);
dFhatdt = zeros (1, tfinal);
dGhatdt = zeros (1, tfinal);
% initial conditions put into the first index of the vectors
Ahat (1) = Ahat_0;
Bhat (1) = Bhat_0;
Chat (1) = Chat_0;
Dhat (1) = Dhat_0;
Ehat (1) = Ehat_0;
Fhat (1) = Fhat_0;
Ghat (1) = Ghat_0;
dAhatdt (1) = dAhatdt_0;
dBhatdt (1) = dBhatdt_0;
dChatdt (1) = dChatdt_0;
dDhatdt (1) = dDhatdt_0;
dEhatdt (1) = dEhatdt_0;
```

```
dFhatdt (1) = dFhatdt_0;
dGhatdt (1) = dGhatdt_0;
% simulation run for small time steps to give concentration over time
for i = 2: tfinal
Ahat(i) = Ahat(i-1) + dAhatdt(i-1);
Bhat(i) = Bhat(i-1) + dBhatdt(i-1);
Chat(i) = Chat(i-1) + dChatdt(i-1);
Dhat(i) = Dhat(i-1) + dDhatdt(i-1);
Ehat(i) = Ehat(i-1) + dEhatdt(i-1);
Fhat(i) = Fhat(i-1) + dFhatdt(i-1);
Ghat(i) = Ghat(i-1) + dGhatdt(i-1);
dAhatdt(i) = -k*Ahat(i)*(Bhat(i)^(c_1));
dBhatdt(i) = -k*Ahat(i)*(Bhat(i)^(c_1)) *c_1;
dChatdt(i) = k*Ahat(i)*(Bhat(i)^(c_1)) *c_2;
dDhatdt(i) = k*Ahat(i)*(Bhat(i)^(c_1)) *c_3;
dEhatdt(i) = k*Ahat(i)*(Bhat(i)^(c_1)) *c_4;
dFhatdt(i) = k*Ahat(i)*(Bhat(i)^(c_1)) *c_5;
dGhatdt(i) = k*Ahat(i)*(Bhat(i)^(c_1)) *c_6;
end
% mols converted to mass of gas produced
mols_of_c = Chat*digester_capacity;
mols_of_d = Dhat*digester_capacity;
mols_of_e = Ehat*digester_capacity;
mols_of_f = Fhat*digester_capacity;
mols_of_g = Ghat*digester_capacity;
mass_of_CO2 = mols_of_c*mm_C;
mass_of_CH4 = mols_of_d*mm_D;
mass_of_NH3 = mols_of_e*mm_E;
mass_of_H2S = mols_of_f*mm_F;
mass_of_H2O = mols_of_g*mm_G;
% fitting factor used to adjust model to experiment
fitting_factor = .0085;
mass_of_CO2_fitted = mass_of_CO2*fitting_factor;
mass_of_CH4_fitted = mass_of_CH4*fitting_factor;
mass_of_NH3_fitted = mass_of_NH3*fitting_factor;
mass_of_H2S_fitted = mass_of_H2S*fitting_factor;
mass_of_H2O_fitted = mass_of_H2O*fitting_factor;
t_fitted = t/ (60*60*24);
pressure_Pa = 101325;
T = 311; %K;
R = 8.314; %J/mol/K
Volume_of_CO2 = (mass_of_CO2_fitted*R*T)/(pressure_Pa*mm_C) *10000;
Volume_of_CH4 = (mass_of_CH4_fitted*R*T)/(pressure_Pa*mm_D) *10000;
Volume_of_NH3 = (mass_of_NH3_fitted*R*T)/(pressure_Pa*mm_E) *10000;
Volume_of_H2S = (mass_of_H2S_fitted*R*T)/(pressure_Pa*mm_F) *10000;
Volume_of_H2O = (mass_of_H2O_fitted*R*T)/(pressure_Pa*mm_G) *10000;
Vol_Biogas =
(0.32*Volume_of_CO2+0.65*Volume_of_CH4+0.1*Volume_of_NH3+0.2*Volume_of_H2S);
plot (t_fitted, Volume_of_CH4,'b', t_fitted, Volume_of_CO2, 'r’, t_fitted,
Volume_of_NH3,'g', t_fitted, Volume_of_H2S,'b', t_fitted, Volume_of_H2O,'r',
t_fitted, Vol_Biogas,'c','LineWidth',1.6)
legend ('CH4 model', 'CO2 model', 'NH3 model', 'H2S model', 'H2O model',
'Biogas Model')
set(gca,'FontSize',12,'FontWeight','bold','linewidth',1.5)
ylabel ('Gas produced (m^3)','FontSize',12,'FontWeight', 'bold')
xlabel ('Retention time(days)','FontSize',12,'FontWeight', 'bold')
Gas_produced=0.04*Dailyinput;
```

```
% Biogas has 22MJ/m3 of calorific value
% Power_available % KW;
Power_available = Gas_produced * (1/3600) * (1/24) * (22*10^6);
% Electricity_production % KWh/year
% Assuming 0.3 electricity converison efficiency
Electricity_production = 0.3 * Power_available * 24 * 365;
% Heat_production % KWh/year
% Assuming 0.55 heat converison efficiency
Heat_production = 0.55 * Power_available * 24 * 365;
```

Appendix−4: - Chemicals Purification Model in g

```
%1. MATLAB SIMULATION FOR 230 Kg/day INPUT
% This code helps to calculate chemical model needed for purification and
amount
% of gas production
%% Sizing of Biogas
prompt = 'Insert Daily input in Kg? ';
Dailyinput = input(prompt);
prompt = 'Insert Retention Time_No of days? ';
RT = input(prompt);
prompt = 'Insert Concentration_of_TS? ';
Concentration_of_TS = input(prompt);
TS=(Dailyinput)*0.3033;
water_required = (TS/Concentration_of_TS)-(Dailyinput);
Total_influent_required = (TS/Concentration_of_TS);
TS=(Dailyinput)*0.3033;
Vgs= 0.5*TS*Dailyinput*0.158;
Vh=Vgs;
%% Kinetic Model
% kinetic coefficient
k = 2.7*10^-6;
% mass flow rate in (kg/day)
dAdtin = 0;
% masss flow rate out
dAdtout = 0;
% these are molar masses of each element
mm_carbon = 12.0107;
mm_hydrogen = 1.0079;
mm_oxygen = 15.999;
mm_nitrogen = 14.0067;
mm_sulphur = 32.065;
% For C_n H_a O_b N_c S_d + H20 => CO2 + CH4 + H2S+ NH3 + H2O
% These constants come from the ultimate analysis
% These constants dictate the coefficients of each term
nbymass = 0.45405;
abymass = 0.07655;
bbymass = 0.42915;
cbymass = 0.03945;
dbymass = 0.004;
% to get molar ratios we divide by molar mass
n = nbymass/mm_carbon;
a = abymass/mm_hydrogen;
b = bbymass/mm_oxygen;
c= cbymass/mm_nitrogen;
d= dbymass/mm_sulphur;
% These are the coefficients in front of each component of the reaction.
```

```
% C_n H_a O_b N_c S_d + c_1* H20 --> c_2*CO2 + c_3*CH4+c_4*NH3 + c_5*H2S +
% c_6*H2O
c_1 = n - a/4 -b/2+(3/4)*c+d/2;
c_2 = n/2 -a/8 + b/4+(3/8)*c+d/4;
c_3 = n/2 + a/8 - b/4-(3/8)*c-d/4;
c_4 = c;
c_5 = d;
%c_6 is 7.5% by mass of the methane gas
c_6 = (0.075*c_3*(mm_carbon + 4*mm_hydrogen))/( 2*mm_hydrogen + mm_oxygen) ;

% These are the molar masses of each component
mm_A = mm_carbon*n + mm_hydrogen*a + mm_oxygen*b+ mm_nitrogen*c+
mm_sulphur*d;
mm_B = 2*mm_hydrogen + mm_oxygen;
mm_C = mm_carbon + 2*mm_oxygen;
mm_D = mm_carbon + 4*mm_hydrogen;
mm_E = mm_nitrogen + 3*mm_hydrogen;
mm_F = 2*mm_hydrogen+mm_sulphur;
mm_G = 2*mm_hydrogen + mm_oxygen;
% These are the masses of each component per mol of food waste
m_A = mm_A;
m_B = c_1*mm_B;
m_C = c_2*mm_C;
m_D = c_3*mm_D;
m_E = c_4*mm_E;
m_F = c_5*mm_F;
m_G = c_6*mm_G;
ratio = m_C/ (m_C + m_D + m_E + m_F + m_G);
% Initial conditions, mass in Kg, digester capacity in m3, volume of reaction
in m3
mass_of_FoodWaste = Dailyinput;
mass_of_water = water_required;
density_of_FoodWaste = 1120;
density_of_water = 1000;
volume_of_reaction = (mass_of_FoodWaste/density_of_FoodWaste +
mass_of_water/density_of_water);
digester_capacity=(Total_influent_required*RT)/(0.8);
Ahat_0 = mass_of_FoodWaste/mm_A/digester_capacity ;
Bhat_0 = mass_of_water/mm_B/digester_capacity ;
Chat_0 = 0;
Dhat_0 = 0;
Ehat_0 = 0;
Fhat_0 = 0;
Ghat_0 = 0;
dAhatdt_0 = -k*Ahat_0*(Bhat_0^(c_1)) ;
dBhatdt_0 = -k*Ahat_0*(Bhat_0^(c_1))*c_1 ;
dChatdt_0 = k*Ahat_0*(Bhat_0^(c_1))*c_2 ;
dDhatdt_0 = k*Ahat_0*(Bhat_0^(c_1))*c_3 ;
dEhatdt_0 = k*Ahat_0*(Bhat_0^(c_1))*c_4 ;
dFhatdt_0 = k*Ahat_0*(Bhat_0^(c_1))*c_5 ;
dGhatdt_0 = k*Ahat_0*(Bhat_0^(c_1))*c_6 ;
%% Can iterate this process for very small steps of time to approximate the
% new concentration of each component of the reaction
% Concentration of each component put into a row vector
tfinal = RT*24*60*60 ;    % retention time : RT
t = (1:tfinal) ;
```

```
Ahat = zeros(1,tfinal) ;
Bhat = zeros(1,tfinal) ;
Chat = zeros(1,tfinal) ;
Dhat = zeros(1,tfinal) ;
Ehat = zeros(1,tfinal) ;
Fhat = zeros(1,tfinal) ;
Ghat = zeros(1,tfinal) ;
% Rate of concentration of each component put into a row vector
dAhatdt = zeros(1,tfinal) ;
dBhatdt = zeros(1,tfinal) ;
dChatdt = zeros(1,tfinal) ;
dDhatdt = zeros(1,tfinal) ;
dEhatdt = zeros(1,tfinal) ;
dFhatdt = zeros(1,tfinal) ;
dGhatdt = zeros(1,tfinal) ;
% initial conditions put into the first index of the vectors
Ahat(1) = Ahat_0 ;
Bhat(1) = Bhat_0 ;
Chat(1) = Chat_0 ;
Dhat(1) = Dhat_0 ;
Ehat(1) = Ehat_0 ;
Fhat(1) = Fhat_0 ;
Ghat(1) = Ghat_0 ;
dAhatdt(1) = dAhatdt_0 ;
dBhatdt(1) = dBhatdt_0 ;
dChatdt(1) = dChatdt_0 ;
dDhatdt(1) = dDhatdt_0 ;
dEhatdt(1) = dEhatdt_0 ;
dFhatdt(1) = dFhatdt_0 ;
dGhatdt(1) = dGhatdt_0 ;
% simulation run for small time steps to give concentration over time
for i = 2:tfinal
Ahat(i) = Ahat(i-1) + dAhatdt(i-1) ;
Bhat(i) = Bhat(i-1) + dBhatdt(i-1) ;
Chat(i) = Chat(i-1) + dChatdt(i-1) ;
Dhat(i) = Dhat(i-1) + dDhatdt(i-1) ;
Ehat(i) = Ehat(i-1) + dEhatdt(i-1) ;
Fhat(i) = Fhat(i-1) + dFhatdt(i-1) ;
Ghat(i) = Ghat(i-1) + dGhatdt(i-1) ;
dAhatdt(i) = -k*Ahat(i)*(Bhat(i)^(c_1)) ;
dBhatdt(i) = -k*Ahat(i)*(Bhat(i)^(c_1))*c_1 ;
dChatdt(i) = k*Ahat(i)*(Bhat(i)^(c_1))*c_2 ;
dDhatdt(i) = k*Ahat(i)*(Bhat(i)^(c_1))*c_3 ;
dEhatdt(i) = k*Ahat(i)*(Bhat(i)^(c_1))*c_4 ;
dFhatdt(i) = k*Ahat(i)*(Bhat(i)^(c_1))*c_5 ;
dGhatdt(i) = k*Ahat(i)*(Bhat(i)^(c_1))*c_6 ;
end
% mols converted to mass of gas produced
mols_of_c = Chat*digester_capacity ;
mols_of_d = Dhat*digester_capacity ;
mols_of_e = Ehat*digester_capacity ;
mols_of_f = Fhat*digester_capacity ;
mols_of_g = Ghat*digester_capacity ;
mass_of_CO2 = mols_of_c*mm_C ;
mass_of_CH4 = mols_of_d*mm_D ;
mass_of_NH3 = mols_of_e*mm_E ;
mass_of_H2S = mols_of_f*mm_F ;
```

```
mass_of_H2O = mols_of_g*mm_G ;
% fitting factor used to adjust model to experiment
fitting_factor = .0085 ;
mass_of_CO2_fitted = mass_of_CO2*fitting_factor ;
mass_of_CH4_fitted = mass_of_CH4*fitting_factor ;
mass_of_NH3_fitted = mass_of_NH3*fitting_factor ;
mass_of_H2S_fitted = mass_of_H2S*fitting_factor ;
mass_of_H2O_fitted = mass_of_H2O*fitting_factor ;
mass_of_H2O_fitted_final=
mass_of_H2O_fitted+(0.4*mass_of_CO2_fitted)+(0.53*mass_of_H2S_fitted);
mass_of_NaOH_fitted = 1.8*mass_of_CO2_fitted;
mass_of_Activated_carbon_fitted = 0.352*mass_of_H2S_fitted;
t_fitted = t/(60*60*24) ;
pressure_Pa = 101325 ;
T = 311 ; %K ;
R = 8.314 ; %J/mol/K
Volume_of_CO2 = (mass_of_CO2_fitted*R*T)/(pressure_Pa*mm_C)*10000;
Volume_of_CH4 = (mass_of_CH4_fitted*R*T)/(pressure_Pa*mm_D)*10000;
Volume_of_NH3 = (mass_of_NH3_fitted*R*T)/(pressure_Pa*mm_E)*10000;
Volume_of_H2S = (mass_of_H2S_fitted*R*T)/(pressure_Pa*mm_F)*10000;
Volume_of_H2O = (mass_of_H2O_fitted*R*T)/(pressure_Pa*mm_G)*10000;

plot(t_fitted, 1.3*mass_of_CH4_fitted/1000,'b', t_fitted,
mass_of_CO2_fitted/1000, 'c',t_fitted,mass_of_NH3_fitted/1000,'g', t_fitted,
mass_of_H2S_fitted/1000,'k', t_fitted, mass_of_H2O_fitted_final/1000,'r',
t_fitted, .76*mass_of_H2O_fitted_final/1000,'y', t_fitted,
mass_of_NaOH_fitted/1000,'m', t_fitted, 1.352*mass_of_H2S_fitted/1000,'k',
'LineWidth',1.6)
legend ('CH4 model', 'CO2 model', 'NH3 model', 'H2S model', 'H2O model',
'Silcagel', 'NaOH', 'Activated Carbon')
set(gca,'FontSize',12,'FontWeight','bold','linewidth',1.5)
ylabel ('Gas produced (g)','FontSize',12,'FontWeight', 'bold')
xlabel ('Retention time(days)','FontSize',12,'FontWeight', 'bold')

Gas_produced=0.04*Dailyinput;
mass_of_NaOH_fitted= 1.8*mass_of_CO2_fitted;
max_mass_of_H2O_fitted_final = max(mass_of_H2O_fitted_final);
max_mass_of_H2S_fitted = max(mass_of_H2S_fitted);
max_mass_of_NaOH_fitted = max(mass_of_NaOH_fitted);
max_mass_of_Activated_Carbon_fitted = max(0.352*mass_of_H2S_fitted/1000);
max_mass_of_CH4_fitted = max(mass_of_CH4_fitted);
disp('=====================================================================')
fprintf ('Gasses produced in g\n')
disp('=====================================================================')
disp('=====================================================================')
fprintf('During the process %g g of CO2 is
produced\n',sum(mass_of_CO2_fitted/1000))
disp('=====================================================================')
fprintf('During the process %g g of CH4 is
produced\n',sum(1.3*mass_of_H2O_fitted_final/1000))
disp('-----------------------------------------------------------------------
----')
fprintf('During the process %g g of H2O is
produced\n',sum(mass_of_H2O_fitted_final/1000))
disp('---------------------------------------------------------------------')
```

```
fprintf('During the process %g g of H2S is
produced\n',sum(mass_of_H2S_fitted/1000))
disp('----------------------------------------------------------------------')
fprintf('To remove the H2O produced, a minimum of %g g of Silica gel is
required\n',sum(1.76*mass_of_H2O_fitted_final/1000))
disp('======================================================================')
fprintf('To remove the CO2 produced, a minimum of %g g of NaOH is
required\n',sum(mass_of_NaOH_fitted)/1000)
disp('======================================================================')
fprintf('To remove the H2S produced, a minimum of %g g of Activated carbon is
required\n',sum(1.352*mass_of_H2S_fitted/1000))

disp('======================================================================')
```