DESIGN, FABRICATION AND OPTIMIZATION OF A SMALL-SCALE ADSORPTION PROCESS REACTOR FOR BIOGAS PURIFICATION

JOHN MAINA CHEGE

A thesis submitted in partial fulfillment for the Degree of Master of Science in Energy Technology in the Jomo Kenyatta University of Agriculture and Technology

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other university.

Signature: _____ Date: _____

John Maina Chege

This thesis has been submitted for examination with our approval as University Supervisors.

Signature: _____ Date: _____

Prof. (Eng.) Bernard.W.Ikua
JKUAT, Kenya

Signature: _____ Date: _____

Dr. Mwangi Njogu
JKUAT, Kenya

Signature: _____ Date: _____

Eng. Njeri Kahiu
JKUAT, Kenya

DEDICATION

This thesis is especially dedicated to my loving family for the love and care you have given me throughout the period of my studies. The support and endurance you have shown, making this thesis much easier to be completed cannot pass unmentioned. Our journey together has not only given me success in this work but has also strengthened my love for all of you. Thank you and may the almighty God repay your generosity abundantly.

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LIST OF ABBREVIATIONS AND ACRONYMS

AD	Anaerobic Digestion
CDM	Clean Development Mechanism
CH_4	Methane
CO_2	Carbon Dioxide
CV	Calorific Value
GC	Gas Chromatography
GHGs	Green House Gases
GoK	Government of Kenya
H_2	Hydrogen
IGCC	Integrated Gasification Combined Cycle
JKUAT	Jomo Kenyatta University of Agriculture and Technology
kPa	Kilo Pascals
LPG	liquefied pressurized gas
MBT	Mechanical-Biological Treatment
N_2	Nitrogen
OSHA	Occupational Safety and Health Act
O_2	Oxygen
ppb	Parts per Billion
ppm	Parts per Million
PSA	Pressure Swing Adsorption
PVC	Polyvinyl chloride
REDDs	Reducing, Emissions, Deforestation and forestation Degradation UN
	United Nations
SNG	Synthetic Natural Gas
SO_2	Sulphur Dioxide
SS	Suspended Solid
TS	Total Solid contents

UNECA	United Nations Economic Commission for Africa
VS	Volatile Solid contents
WHO	World Health Organization

ABSTRACT

Biogas is a renewable energy resource. Emissions from biogas can cause serious damage to the human health and environment due to presence of the contaminants. The aim of this study was to evaluate biogas generation from cattle dung and developing a purification system for biogas in small-scale farms before utilization. Currently, biogas purification occurs in large scale plants. Biogas which is produced in an anaerobic digestion process consists of methane (CH_4), carbon dioxide (CO_2), small amounts of water vapour together with traces of hydrogen sulphide (H_2S) and other impurities. The presences of H_2S and CO_2 have detrimental effects on health, burning apparatus and the calorific value of biogas. Reducing these impurities will significantly improve the quality of the gas. Biogas samples were collected in small bags from three digesters located in Ongata Rongai division of Kajiado County about 20 km west of Nairobi City. It was analysed in the laboratory for the concentrations of CH_4, CO_2, H_2S, oxygen (O_2) and nitrogen (N_2). Investigations were performed using chemical adsorption for removal of H_2S and H_2O and chemical absorption for CO_2. The purification system comprised three columns charged with ferric oxide, calcium hydroxide solution and silica gel to scrub H_2S, CO_2 and water (H_2O) respectively. The biogas was passed through the charged columns and the operating parameters mainly contact time and flow rate studied for the contaminants removal from the biogas stream in each column separately. The results show that the initial average concentration 0.0052 ± 0.02% H_2S was reduced to 0.0012 ± 0.01% when a flow rate of 20 litres/min of biogas is maintained after passing biogas through the derived ferric oxide adsorbent material. The concentration of CO_2 in the biogas for the same flow rate was reduced from an average of 46% to 30 ± 2%. The CH_4 concentration realized at saturation of calcium hydroxide ($Ca(OH)_2$) solution was 60 ± 4%. This represented a 20 ± 3% improvement in the CH_4 content from the initial average value of 48.5 ± 2%. The improvement in the heating value of the gas was found to be 66%. The results confirmed the potential of the packed column design for biogas contaminants removal and heating value improvement using the adsorption process utilizing ferric oxide, calcium oxide and silica gel.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background Information

Renewable energy derived from biomass sources has great potential for growth in meeting future energy demands. Biogas is one of the most important renewable energy and an indigenous source as it is widely available (Tippayawong &Thanompongchart, 2010). It comprises of a flammable mixture of different gases that are produced by decomposition of biodegradable organic matter by mechanical-biological treatment (MBT) process known as anaerobic digestion (AD) (Chaundhary, 2008). The main gaseous products are methane (CH_4), carbon dioxide (CO_2) and traces of small amounts of other contaminants (Hullu *et al*., 2008). A typical composition of biogas is as given in Table 1.1.

Table 1.1 Typical Biogas Compositions

Component	Composition (vol. %)
CH_4	55 – 65
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
CO	0.001 – 2
NH_3	Trace
Organics	Trace

Source: Bori *et al*., 2007

The ever increasing global energy demand has necessitated research in new renewable energy technologies that aim at producing clean power. Biogas being a clean, cheap and environmentally friendly fuel stands out as one of them. For Kenya to achieve its target of becoming industrialized nation by 2030, a reliable supply of quality energy is crucial (GOK, 2008). Interest in bio-fuels has been increasing, motivated on one hand by the need for reducing greenhouse gases (GHG) emission and on the other hand by the desire to improve energy security by reducing dependence on largely imported fossil fuels. The government has enacted a policy (GOK, 2004) and legislation (GOK, 2006) which seeks to ensure sufficient biomass supplies to meet demand on a sustainable basis while minimizing the associated impacts. Majority of people living in the rural areas use biomass, mainly wood derived fuel as the source of energy for cooking and lighting. However, the potential of biogas has not been effectively utilized in the provision of energy. Continued over-dependence on the unsustainable wood derived fuel and other forms of biomass to meet household energy needs has contributed to deforestation with negative impacts on the environment.

Biogas has the potential to counteract many adverse health and environmental impacts connected with traditional biomass energy. Besides supplying energy and manure, biogas usage can provide an excellent opportunity for mitigation of GHG emission and reduction of global warming. The Clean Development Mechanism (CDM), an arrangement under the Kyoto Protocol on the emissions reduction projects in developing countries singles out biogas as a potential renewable energy replacement for kerosene in the rural areas (UNECA, 2011). The United Nations (UN) program of Reducing Emissions from Deforestation and Degradation (REDDs) is a recommended initiative for developing countries in reducing emissions from forested lands and invest in low-carbon paths such as biogas (Smith, 2011).

In the Kenyan market the major application of biogas has been in cooking, lighting, heating and drying at the domestic scale mainly in the rural areas. Once produced, the

flow of the biogas to the burners is due to pressure built up in the digester which is only sufficient to serve the surrounding areas. However, biogas has been found to contain some impurities of concern as noted by Lise *et al*., (2008). Some of them particularly H_2S have detrimental effects on burning apparatus, and environment pressure regulators, gas meters, valve mountings and engine parts. As noted by the World Health Organization (WHO), the emissions from indoor burning of unprocessed biomass are a serious health hazard (Pardey, 2012). The presence of CO_2 lowers the Calorific Value (CV) of the gas as it does not support combustion, while the entrained water vapour present in carrier pipelines causes corrosion and fouling of the burners. The CV of biogas is between 20 – 28 MJ/m^3 depending on the CH_4 content while that the liquefied pressurized gas LPG is 39 MJ/m^3 (Cebula, 2009). In order to meet the requirements for a clean gas by increasing the level of CH_4 concentration, the biogas must go through a purification process (Wargert, 2009).

1.2 Problem Statement

All biogas streams commonly contain harmful impurities, such as CO_2 and H_2S. These impurities 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 vapour. 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. Today, there is no economically viable technology capable of purifying biogas for small-scale biogas digester installations. Purification technologies have only been developed for large municipal wastewater treatment plants mainly found in developed countries. The installations are highly

mechanized and are largely high capital investments.

As a result of such limitation, this research study led to the consideration of development of a purification system with a view to improve the quality of biogas for effective utilization in small scale installations. Thus, the purification system being developed will be a simple and a robust purifier meeting the requirements of continuous removal of H_2S, CO_2 and H_2O from the biogas while maximizing the CH_4 content. This will consequently improve the calorific value of the biogas.

1.3 Study Objectives

1.3.1 Main Objective

The main objective is to develop a small scale chemical adsorption reactor for biogas purification.

1.3.2 Specific Objectives

The specific objectives are to:

i. Determine the total and volatile solids.
ii. Analyze the biogas composition.
iii. Test the performance of biogas purification reactor.
iv. Establish the heating value of the reactor.

1.4 Null Hypothesis

Purification of biogas cannot improve the gas performance.

1.5 Justification

The research will benefit the farmers who are looking forward to installing systems that utilize biogas as an energy source. The designers and operators of other agricultural facilities, landfills, and wastewater treatment plants, food processing facilities and generally where renewable bio-based energy can be produced will also benefit from this design. The design will also enable the production of more clean energy that will mean that less fossil fuel will be burned for energy and as a result smaller amounts of harmful gases will be released into the atmosphere. The reduction in global warming will encourage policy makers to promote biogas technology to combat climate change and integration of carbon revenues will help the farmers to develop biogas as a profitable activity. It is hoped that this study will aid farmers, engineers, government authorities and students to pursue the advancement of renewable energy projects and to encourage further development of upgraded biogas as an alternative to using nonrenewable natural gas.

CHAPTER TWO

2.0 LITERATURE REVIEW

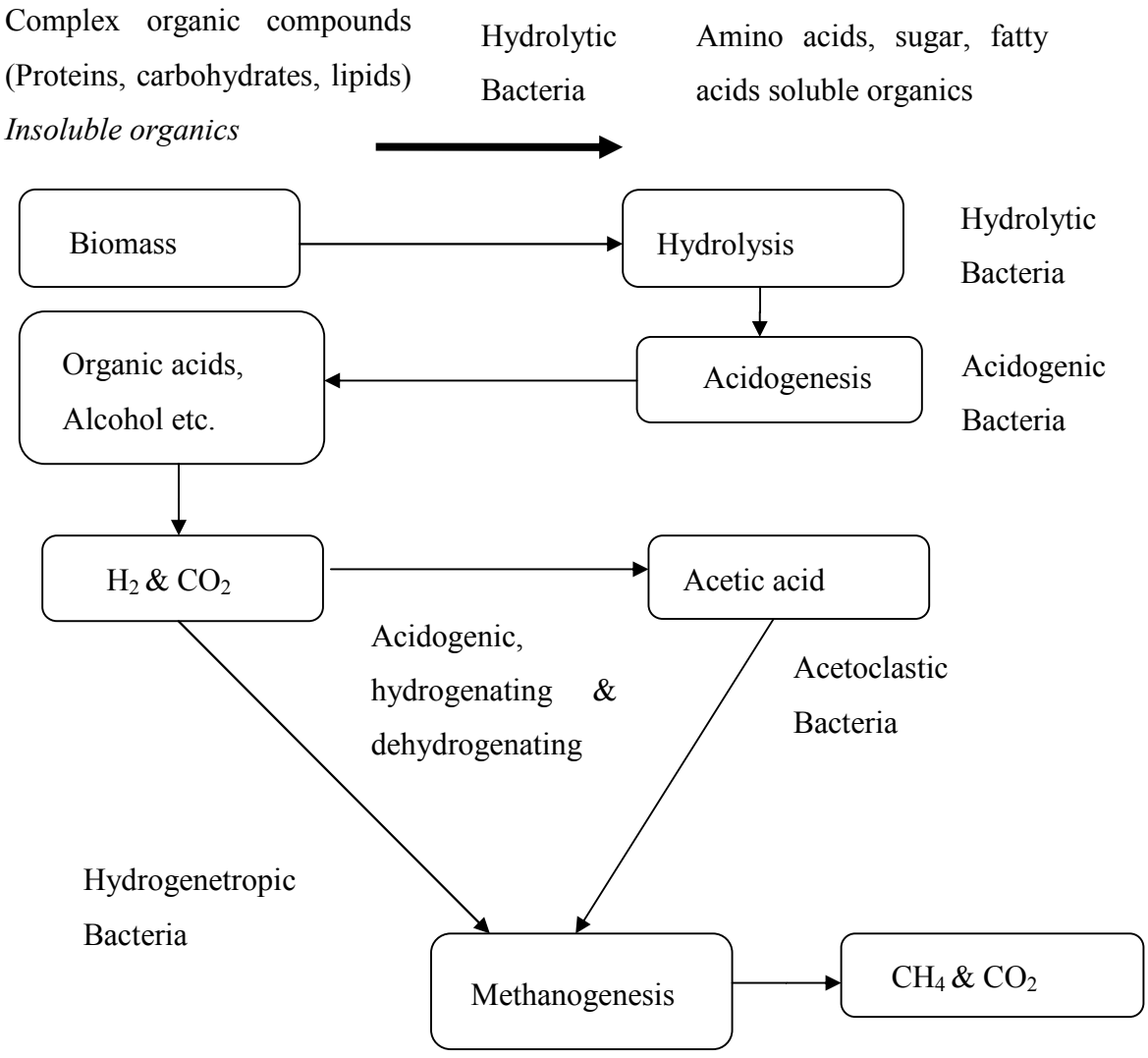
2.1 Introduction

There have been few reports on biogas purification and upgrading especially in small-scale applications. A great deal of previous studies has focused on large equipment for biogas upgrading systems. According to Eze and Agbo, (2010) majority of such studies were carried out on water scrubbing systems, which is the simplest and cheapest method involving the use of pressurized water as an absorbent. It is possible to produce high quality CH_4 enriched gas from biogas using chemical absorption where a packed bed column and buddle column are used to provide liquid/gas contact. However, there are several drawbacks of using liquid solutions for CO_2 and H_2S removal. These include high energy requirement for regeneration, stability and selectivity of chemicals used, environmental impact from waste liquids, requirement for large equipment and high corrosion rates.

Purification of biogas is an important process in the utilization of this energy as reported by Greer (2010). Biogas generated from AD 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). For small systems, sulphur scavenging process which are group of processes which acts as a non-regeneration manner to remove small quantities of sulphur compounds have been in use. They are made up of solid materials which capture and retain sulphur compounds. The materials have relatively short lifespan and when they become saturated they require removing and replacing. This chapter reviews the composition of biogas with the associated environmental impacts and evaluates the primary purification methods and their characteristics with suggestions on the most practical processes for small scale applications.

2. 2 Biogas Production

The production of the biogas involves complex chemical and biological processes that are dependent on different factors and stages of change in a system known as a digester. Figure 2.1 shows the subsequent chemical stages during the production process.



Source: Chaudhary, 2008

Fig. 2.1: Degradation pathways in Anaerobic Digestion

In the first stage the hydrolytic bacteria are involved in the breakdown of complex organic waste into simple sugars, fatty acids and amino acid. The Acidogenic bacteria then convert the organic acids into hydrogen, acetate and CO_2. During the final stage the CH_4 producing bacteria Methanogens; simultaneously produce biogas from acetate or from hydrogen and carbon dioxide. CH_4 is the principal constituent of biogas and is the only part that is considered as essential. It is a light, colorless and highly inflammable gas second only to hydrogen in the energy content per gram of fuel burnt.

Anaerobic digestion processes can be applied to clean high-concentration waste waters from food processing industries, to produce energy from the organic fraction of municipal waste or from animal waste slurries. Due to the different properties of the substrates, there are special digester configurations and operation modes for each application. Depending on the raw material and the digestion process, the composition of the biogas produced will vary. Table 2.1 shows the typical range of CH_4 contents for different ingredients for the production of biogas.

Table 2.1 Range of CH_4 content from Different Materials

Biogas Derivative	Methane Content [vol/vol%]
Agricultural wastes	55 – 75
Sewage sludge	60 – 70
Organic high-concentration waste waters	50 – 85
Organic fractions of municipal waste	55 – 65
Municipal waste in landfills	35 – 60

Source: Kishore & Srinivas, 2003

In Kenya, small scale digestion plants are run on animal manure which is the major biomass resource. Some of these biogas plants are fed with additional organic wastes from agriculture while others with food processing refuse to increase biogas production.

2. 3 Contaminants in Biogas

The removal of contaminants from biogas is of crucial importance to guarantee better performances in biogas exploitation processes and to reduce environmental impact of gaseous emissions. Some of the contaminants in biogas are water vapour, CO_2 and H_2S and need to be removed before using the gas in the appliances.

2. 3.1 Water Vapour

The need to remove H_2O from biogas is done for various reasons including protecting equipment from corrosion, need to increase the CV and for the purpose of standardizing the biogas (Lise *et al*., 2008). Water vapour is present in proportions varying from 5% to saturation and combines with H_2S and CO_2 to form sulfuric acid and mild carbonic acid respectively (Electrogaz, 2008). During the combustion of biogas, H_2O causes the lowering of flame temperature, heat values and the stoichiometric or air-fuel ratio of gas. Removal of water vapour from biogas leads to a reduction in the possibility of corrosion of metallic components, an increase in the heat value of biogas by as much as 10% as well as increases in both the flame temperature and air fuel ratio (Jaffrin *et al*., 2003).

2. 3.2 Carbon Dioxide

Incombustible CO_2 reduces the CV of biogas, increases its handling requirements and reduces its flame velocity (Lise *et al*., 2008). The content of CO_2 which varies as a function of conditions prevailing in a digester and the digester feed composition, introduces constraints on the efficient operation of appliances, such as gas burners (Electrogaz, 2008). It is therefore, important where possible to remove the gas from the biogas before storage or use.

2. 3.3 Hydrogen Sulphide

Kuria and Maringa (2008) reported H_2S levels in biogas in the range between 0.001 – 0.4% v/v. This gas is corrosive and reduces the life of metals appliances such as copper, iron, steel and lead pipes, gas holders and other metallic accessories if not removed from the biogas (Horikawa *et al*., 2004). H_2S concentration of up to 1% coupled with CO_2 concentration above 2% is particularly corrosive. Tippayawong and Thanompongchart (2010) in their research paper have reported that the concentration of H_2S of more than this level should be removed from the biogas before use.

H_2S has an undesirable pungent smell or odor and is toxic in proportions above 10 ppm. The effects of H_2S exposure causes eye irritation and is considered a poison in concentration about 10 - 50 ppm. Continuous exposure to concentration of H_2S of between 10 - 50 ppm gives rise to nausea, dizziness, headaches and irritation of mucous membrane, while exposure to concentration of about 200 – 300 ppm will lead to respiratory arrest, comma or unconsciousness Scrully *et al*., 2007). Exposure to concentration of H_2S in excess of 700 ppm for periods longer than 30 minutes is likely to result into pulmonary paralysis, sudden collapse and death (Syed *et al.,* 2006). When oxidized, H_2S form SO_2 and SO_3 both of which are even more poisonous than H_2S. The two oxides form the very highly corrosive sulfuric acid when exposed to water and may occur in the environment as acid rain (Abatzogluo, 2008).

Consequently, the H_2S removal is necessary particularly at the gas production site. Table 2.2 shows the physical, chemical and safety characteristics of H_2S. For gas used in kitchen stoves, the H_2S should be less than 10 ppm as the biogas is being used just for cooking (Eze and Agbo, 2010).

Table 2.2 Physical, Chemical and Safety Characteristics of H_2S

Characteristics of H_2S	
Molecular Weight	34
Specific Gravity (relative to air)	1.192
Auto Ignition Temperature	250 °C
Explosive Range in Air	4.5 to 45.5%
Odor Threshold	0.47 ppb
8-hour time weighted average	10 ppm
15-minute short term exposure limit	15 ppm
Immediately Dangerous to life of Health	300 ppm

Source: Sujans *et. al*., 2011

2. 4 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. Biogas quality standards vary by application. Table 2.3 is a summary of potential utilization technologies and the gas processing requirements.

Table 2.3 Biogas Utilization Technologies and Gas Processing Requirements

Technology	Recommended Gas Processing Requirements
Heating (Boilers)	H_2S < 1000 ppm, 0.8 – 2.5 kPa pressure, remove condensate (Kitchen stoves: H_2S < 10 ppm)
Internal Combustion Engines	H_2S < 1000 ppm, 0.8 – 2.5 kPa pressure, remove condensate and siloxanes (Otto cycle engines more susceptible to H_2S than diesel engines)
Microturbines	H_2S tolerant to 70,000 ppm,>350 BTU/scf, 520 kPa pressure, remove condensate, remove siloxanes
Stirling Engines	Similar to boilers for H_2S, 1-14 kPa pressure
Natural Gas Upgrade	H_2S < 4 ppm, CH_4 > 95%, CO_2 < 2% volume, H_2O < (1 x $1O^{-4}$) kg/MMscf, remove siloxanes and particulates, > 3000 kPa pressure

Source: Chaudhary, 2004

2. 4.1 Biogas Energy Potential and its Natural Gas Equivalent

Table 2.4 shows the composition and physical properties of natural gas and biogas. It can be seen that CH_4 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 2.4 Physical Properties of Natural Gas and Biogas

Key numbers	**Unit**	**Natural gas**	**Biogas**
CH_4 (methane)	vol%	91.0	55 - 70
CO_2 (carbon dioxide)	vol%	0.61	30 - 45
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	°C	2040	1911

Source: Zhou *et al*., 2011

Generally, upgraded biogas or synthetic natural gas (SNG) is considered compatible with natural gas if its Wobbe Index is within ± 10% of the Wobbe Index of natural gas (Zhou *et al*. 2011). By removing CO_2, the Wobbe index of biogas can be increased to that of natural gas quality. Because of its corrosive and hazardous properties, H_2S comprising between 100 – 50,000 ppm must also be removed before biogas can be introduced to a natural gas pipeline.

2. 5 Cleaning and Upgrading Technologies

In order to improve the quality of biogas from AD it must pass two major processes:

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

The relevance and feasibility of the different types of cleaning and upgrading processes depends on the specific biogas composition, which is dependent on the biomass feedstock and the digestion process (Greer, 2010). Thus the two major steps are not always totally separated. Biogas cleaning and upgrading technologies utilize a range of passive media, chemicals and biological treatment techniques. These methods differ in the effectiveness, capital costs, operating costs and operational complexity. The following section describes processes that have been developed in upgrading and cleaning the biogas to improve quality.

2. 5.1 Removal of Hydrogen Sulphide

Proteins and other sulphur containing materials in the feedstock produce H_2S in the digestion process. H_2S is poisonous and corrosive, as well as environmentally hazardous since it is converted to SO_2 by combustion. The gas can be removed either in the digester, from the crude biogas, or in an upgrading process. There are numerous methods used to remove H_2S from the biogas systems and are categorized in groups as follows (Tjokorda *et al*., 2013):

i. Absorption into a liquid either water or caustic solution.
ii. Adsorption on a solid such as iron oxide - based materials, activated or impregnated carbon.
iii. Biological conversion by which sulphur compounds are converted into elemental sulphur by sulfide oxidizing micro organisms with addition of air/oxygen.

2.5.1.1 Absorption of H_2S into a Liquid either Water or Caustic Solution

Liquid based processes require significantly higher capital, energy and media costs, although regeneration is possible. In his work, McKinsey (2003) has noted that commercial biological processes for H_2S removal are also available and claim to effectively reduce operating, chemical and energy costs but require higher capital costs than dry based processes. Of the many processes currently employed that have been in use for large-scale desulphurization of technical gases, only the so-called dry processes are suitable on a smaller scale for biogas plant. They are acceptable from the point of view of their technical simplicity and maintenance and also the high degree of purification they provide. This therefore leaves the dry oxidation purification process as the best option for small biogas systems.

2.5.1.2 Removal of H_2S using Metal Oxides and Hydroxides

This is a process involving chemical adsorption of H_2S on solid adsorbents. The most commonly used adsorbent is iron oxide, but iron hydroxide and zinc oxide can also be used. The biogas is passed through iron oxide pellets to remove H_2S. When these pellets are completely covered with sulphur they are removed and regenerated (Navaratnasamy, 2008). Rusty steel wool and ferric oxides in the form of iron sponge with wood shavings are the simplest and the most economical methods involving the use of iron oxide. However, although steel wool is cheap it has a relatively small surface area which results in low binding capacity for the sulfide. The reaction requires water and therefore the biogas should not be dried before this stage. Condensation in the iron sponge should be avoided since water can bind iron oxide materials.

$$2Fe_2O_{3\,(s)} + 6H_2S_{\,(g)} \longrightarrow 2Fe_2S_{3\,(s)} + 6H_2O_{\,(l)} \qquad (2.1)$$

$$2Fe_2S_{3\,(s)} + 3O2_{\,(g)} \longrightarrow 2Fe_2O_{3\,s)} + 6S_{(s)} \qquad (2.2)$$

Like all gas-solid adsorption processes, iron-sponge – based H_2S removal is operated in

batch mode with separate regeneration, or with a small flow of air in the gas stream for continuous or at least partial regeneration. The iron sponge can be operated in batch mode with separate regeneration. In the batch mode, only about 85% (0.56 kg H_2S/kg Fe_2O_3) of theoretical efficiency can be achieved (Abatzoglou, 2008). The same author reported that regeneration takes place under the following conditions: 8% vol.O_2 concentration in the gas stream and at space velocity 0.3 – 0.6 m^3/m^3 of the iron sponge/min. Alternatively, the sponge can be removed, spread out in a 0.15 m-thick layer, and continually wetted for 10 days. Removal rates as high as 2.5 kg H_2S/kg Fe_2O_3 have been reported in continuous-regeneration mode with a feed-gas stream containing only a few tenths of a percent of oxygen (Abatzoglou, 2008).

Design parameter guidelines have been established for optimum operation. Mckinsey (2003) presented a collection of these criteria as shown in Table 2.5 considering that the biogas to be purified has the following characteristics at 25 °C and gauge pressure being lower than 2 bars from the digester.

Table 2.5 Design Parameter Guidelines

Biogas composition:	60% CH_4, 40% CO_2
H_2S content	4000 ppm
H_2O content	Saturated biogas
Biogas flow rate	1400 m^3/day
Adsorbent useful lifespan	20-80 days
Annual Iron sponge consumption	4 – 16 tonnes

Source: Mckinsey, 2003

H_2S levels at one farm digester were consistently reduced from a high as 3600 ppm to below 1 ppm with a 1.5 m diameter x 2.4 m deep iron sponge reactor.

Regeneration involves exposing the iron sponge to air (oxygen) which converts the ferric sulfide formed by the scrubbing operation back to ferric oxide and elemental sulphur. One problem with this technology is that the regenerative reaction is highly exothermic and can, if air flow and temperature are not carefully controlled, result in self-ignition (Cherosky, 2012). For a small farm application requiring both H_2S and CO_2 removal and compression of the biogas, the iron sponge technology using iron-impregnated wood chips appears to be most suitable. The process is used almost exclusively for the treatment of relatively small volume of gas, where the amount of sulphur does not justify the expense and complexity of a regenerative process.

Currently, iron oxide media that include Sulfa Treat®, Sulfur-Rite® and Media-G2® have been offered as improved alternatives to iron sponge (Mckinsey, 2003). These have greater surface areas and are efficient (Greer, 2006). A mixture of iron oxides, with the Sulfa Treat® which is based on a naturally occurring substance and is in form of granules, is used in reaction beds for the same purpose. It mainly consist of Fe_2O_3 or Fe_3O_4 compounds coated with granulated support and is used just like iron sponge in a low pressure vessel with down-flow of gas and is effective with partially or fully hydrated gas stream. With a downstream gas flow the water is better distributed in the bed. The gas flow is saturated with water and excess water is added to the reaction bed. Reaction temperature is dependent on the H_2S content in the biogas. With fresh SulfaTreat® and moderate concentrations of H_2S, all the gas is removed. The bed material is consumed by the reaction and this result in a rising H_2S content in the outlet stream. If it is important to keep the H_2S content in the cleaned gas to virtually zero, gas sampling can be done in the bed at some distance from the gas outlet. When the H_2S content increases in the sample, the bed material is removed and the reactor is recharged with fresh material. For completely continuous running, two reactors can be installed and switched when the H_2S content starts to increase.

Sulfa Treat® has multiple benefits over iron sponge due to its uniform structure and

free-flowing nature (McKinsey, 2003). It does not pose safety hazard during change out but a big drawback associated to this product is that the process is non-regenerable and chemically intensive. A two vessel arrangement (series) is proposed by Sulfa Treat Company to ensure maximum removal.

Sulphur-Rite® is also a dry-based iron-oxide product. The end product after adsorption is iron pyrite. Sulphur-Rite® system comes in prepackaged cylindrical units that are recommended for installations with less than 180 kg sulfur/day in the gas and flow rates below 70 m^3/min. It also has many of the disadvantages of the iron oxide scavenger. Media-G2® is an iron-oxide based adsorption technology. Laboratory scale and pilot scale trials indicates that treatment of up to 30,000 ppm H_2S is possible, spent product is non-hazardous and Media-G2® can remove up to 560 mg H_2S/g solid. A two vessel system design (parallel) is recommended for continuous operation.

Another proprietor product Sulfa Master® has been designed for removal of H_2S from gases generated in wastewater treatment from biogas used in bio-energy production. This product has the ability to reduce H_2S concentration from 30,000 ppm to below detectable levels (Frare *et al*., 2009). The media base is dried dairy manure and the absorption element is iron. The pH is 7-8 and the reaction that occurs is as follows:-

$$Fe^{2+}_{(aq)} + H_2S_{(g)} \longrightarrow FeS_{(s)} + 2H^{+}_{(aq)} \quad (2.3)$$

$$Fe_2O_3.H_2O_{(s)} + 3H_2S_{(g)} \longrightarrow Fe_2S_{3\,(s)} + 4H_2O_{(aq)} \quad (2.4)$$

The product has shown results of low cost and efficient method for H_2S removal and the spent material can be disposed off easily by spreading. The manure is totally biodegradable and under aerobic soil conditions, the free sulphur will be converted into sulphate.

The other substance in this category is silica gel which is a desiccant that absorbs moisture and other materials from a gaseous environment (Maat *et al*., 2009). In a study completed by Electrogaz, (2008) to selectively remove H_2S from biogas, the result

showed that under the right circumstances such as flow rate, silica gel absorb sulphur compounds as well as moisture and by running the contaminated CH_4 through a column of silica gel removes H_2S.

2. 5.1.3 Removal of H_2S by Adsorption on Activated Carbon – (Impregnated)

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. The main chemicals serving as impregnates are sodium bicarbonate ($NaHCO_3$), sodium hydroxide (NaOH), potassium hydroxide (KOH), potassium iodide (KI), and potassium permanganate ($KMnO_4$). However, Kaczmarczyk *et al*., (2010) found that caustic modified active carbons easily undergo self-ignition and as a result this strongly limits their application. Rather, mixtures of these chemicals are sometimes used. A typical H_2S loading capacity for caustic, impregnated carbons is 0.15g/g of activated carbon (Abatzoglou, 2008). Strong base-impregnated carbons are regenerable by re-application of strong base. Adsorption on activated carbon removes even small quantities of sulphur from biogas. The carbon loaded with sulphur can be replaced with fresh one or regenerated. From this point of view it is important to ensure high quality of activated carbon for sulphur adsorption from biogas. CO_2 in the raw biogas adsorbs into the surface of a solid materials known as molecular sieves (Ryckebosch *et al*., 2011). The solid adsorbents used for purification of gas include among others, carbon and silica. H_2S can be adsorbed on activated sieves.

There are three basic types of activated carbon namely catalytic-impregnated, impregnated carbons and non-impregnated carbon. Catalytic activated carbon is manufactured by treatment with urea or some other chemicals containing nitrogen. These chemicals react with the surface sites on activated carbon particles. According to

Norit Americas, Inc. (2007) fresh catalytic system has achieved H_2S loading capacities of around 0.1g/g of activated carbon. Catalytic carbons are said to be water-regenerating. Sulphur containing carbon can then either be replaced with fresh activated carbon or regenerated. The adsorption of H_2Son activated carbon is catalytic and the carbon acts as catalyst (Hagen *et al*., 2001). The chemical reaction is:

$$2H_2S_{(g)} + O_{2\,(g)} \longrightarrow 2S_{(s)} + 2H_2O_{\,(l)} \qquad (2.5)$$

O_2 is needed for the reaction and is usually added as air. This result in N_2 being the gas, but if the H_2S content is low, only minor amounts of N_2 will be present in the cleaned gas. If the carbon is regenerated, this is done with hot N_2 (inert gas) or steam (Navaratnasamy, 2008). The sulphur will be vaporized and, after cooling, liquefy at approximately 130 °C. Regeneration requires two reaction vessels for continuous running. Adsorption systems are simple in design and easy to operate (Kapid *et al*., 2004). However the high heat and pressure required make them expensive processes. The most common way for utilizing activated carbon adsorption is without regeneration of the carbon.

2. 5.1.4 Removal of H_2S by use of Sludge-Derived Absorbents

Sludge coming from biological activity is quite a complex mixture of organic matter. Its ability to chemically adsorb H_2S from gaseous streams has been examined by a limited number of researchers. Recent research carried out by Sayyadnejad *et al*., (2008) found that various absorbents have been used in industry to remove H_2S from different media. Zinc compounds such as Zinc Oxides (ZnO) and Zinc Carbonate are common scavengers to remove H_2S (Davidson, 2004). ZnO is a candidate for the removal because it has high zinc content and has well predictable reaction kinetics and absorption capacity. It is also readily available compared with other absorbents. H_2S absorption by ZnO is actually controlled by the following reaction that forms inert insoluble Zinc sulfide (Fang, 2006).

$$ZnO_{(s)} + H_2S_{\,(g)} \longrightarrow ZnS_{(s)} + H_2O_{(l)} \qquad (2.6)$$

The ZnS is then disposed off as it is a non-regenerative process. The efficiency of this system is close to that of iron adsorbents but it is less than that of impregnated carbon (Abatzoglou, 2008).

2. 5.1.5 Removal of H_2S in Digesters

H_2S can be removed directly in the digester vessel (Hagen *et al*., 2001). The gas is either reacted with a metal ion to form an insoluble metal sulfide or oxidised to elementary sulphur. Iron salts are the most used reactants for the reduction of H_2S emissions. Iron, reacts with sulfide ions to form iron sulfide (FeS). Further research (Saelee *et al*., 2009) showed that Iron ion is normally supplied as iron chloride, ($FeCl_2$), which is added to the digester.

$$Fe^{2+}_{(s)} + H_2S_{(g)} \longrightarrow FeS_{(s)} + H_{2\,(g)} \qquad (2.7)$$

H_2S levels of typically 100 to 150 ppm in the gas stream can be reached with this method. The removal of H_2S is included in the turn key biogas plant or installed by the plant owner. The investment costs are rather low since the only equipment needed is a dosing system. On the other hand the operational cost for this method depends on the amount of H_2S that is formed by the digestion processes. When using raw materials that are rich in protein and other sulphur containing molecules, this method is rather expensive.

2. 5.2 Removal of Water from Biogas

Biogas from digesters is normally collected from headspace above a liquid surface or very moist substrate making the gas usually saturated with water vapour. The amount of saturated water in the gas depends on temperature and pressure in the digester. H_2O from the biogas can be removed in a number of ways: -

2. 5.2.1 Removal of Water from Biogas by Adsorption

Adsorptive drying means that H_2O is adsorbed on the surface of a drying agent. Silica gel, aluminium 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.

Regeneration can be performed in two different ways. If the drying is performed at elevated pressure, a minor amount (3 - 8%) of the dried gas can be depressurized and used for regeneration. This gas is then recycled to the compressor inlet which means that the net capacity of the compressor is lowered. If drying is performed at atmospheric pressure the regeneration is performed with air and a vacuum pump. This method has the disadvantage of mixing air into the gas and is therefore not well suited for the drying of biogas (Hagen *et al*., 2001).

2. 5.2.2 Removal of Water from Biogas by Absorption

Water can be absorbed into chemicals such as glycol or triethylene glycol or hygroscopic salts (Hagen *et al*., 2001). There are many types of salts with different absorption properties. Normally the drier consists of an absorption vessel filled with salt granules. The wet gas is fed from the bottom and the salt is dissolved as it absorbs water. The saturated salt solution is withdrawn with a valve from the bottom of the vessel. The salt is not regenerated and new salt granules have to be added to replace the dissolved salt or pumped into a regeneration unit to be regenerated by heating to a temperature of approximately 200 °C (McKinsey, 2003). The dew point lowering for commercial driers is typically in the interval 10 to 15 °C depending on the salt.

2.5.3 Carbon Dioxide Removal from Biogas

CO_2 is a major component in the raw biogas and the vast majority of it is removed in the upgrading process in order to raise the CV, Wobbe index etc. However, traces of CO_2 will be present in the upgraded gas. Therefore the upgrading process is basically a separation of the CH_4 and CO_2 of the biogas, in order to obtain gas quality with regards to CV, Wobbe index, relative density etc. The following upgrading processes are available in removing CO_2:

i. Membrane separation
ii. Pressure Swing Adsorption (PSA)
iii. Absorption without chemical reaction
iv. Absorption with chemical reaction
v. Cryogenic removal of CO_2
vi. Adding propane (supplementary upgrading)

These processes though highly effective are either too expensive or technically infeasible for small scale systems. Alternative methods for CO_2 removal include using suitable chemicals such as Calcium Oxide (CaO), Calcium Hydroxide ($Ca(OH)_2$) and Ammonium Hydroxide (NH_4OH). CO_2 is an acidic gas as it forms carbonic acid (H_2CO_3) upon dissolving in water. Hence for absorption of CO_2 gas suitable bases have to be used to result an acid-base neutralization reaction thereby absorbing and reducing the CO_2 content in the biogas.

2.5.3.1 Removal of Carbon Dioxide from Biogas using Selexol

For physical absorption, CO_2 is physically absorbed in a solvent according to Henry's Law, which means that they are temperature and pressure dependent with absorption

occurring at high partial pressures of CO_2 and low temperatures. The solvents are then regenerated by either heating or pressure reduction. The advantage of this method is that it requires relatively little energy; but the CO_2 must be at high partial pressure. Hence, it is suitable for recovering CO_2 from Integrated Gasification Combined Cycle (IGCC) systems where the exhaust CO_2 would leave the gasifier at elevated pressures. Typical solvents are Selexol (dimethylether of polyethylene glycol) and Rectisol (cold methanol). Selexol is registered trade mark for polyglycol ether. The scrubbing process relies on the same underlying mechanism as H_2O and H_2S is more soluble than CH_4 in the solvent. The chemical is dissolved in H_2O and has a very low vapour pressure. This means that the losses of chemicals are very low in the process. Wellinger and Lindeberg (1999) have reported that selexol removes CO_2, H_2S and H_2O simultaneously. The selectivity for H_2S is very high compared to CO_2 and regeneration from H_2S requires increased energy input. CO_2 is absorbed in a circulating selexol solution at elevated pressure. Cleaned biogas is compressed and fed into the bottom of an absorption column. Selexol is fed from the top of the column to achieve a gas-liquid counter flow. The column is equipped with random packing to give a large surface for gas-liquid contact and internals for the collecting and redistribution of selexol. CO_2 is absorbed by the selexol solution and the gas leaving the top of the column is stripped from most of the CO_2 content. CH_4 is partly soluble in pressurized selexol solution and therefore some of it will be removed with the liquid. To minimize the losses, the selexol solution is depressurised in a flash tank after leaving the absorption column. The released gas mixture is rich in CH_4 and is re-circulated to the compressor inlet. The major drawback is that this process is more expensive for small-scale application than scrubbing or PSA.

2.5.3.2 Removal of Carbon Dioxide from Biogas by Chemical Reaction

In this process, raw gas is led through a liquid, typically at elevated pressure and temperature, and the undesired components (e.g. CO_2, H_2S) are absorbed in the liquid.

However, instead of simply dissolving these components, the liquid reacts chemically with them and therefore drives them into solution (Hagen *et al*., 2001). Due to the high costs of the absorber material it is always regenerated. The process is continuous and the absorber is regenerated in a reversal chemical reaction in which the absorbed CO_2 is released. The greatest limitation for CO_2 recovery from biogas is the low pressure of the gas. CO_2 is absorbed much more easily into solvents at high pressure. The only commercially available solvents that can absorb a reasonable amount of CO_2 from dilute atmospheric pressure gas are primary hindered amines, such as MEA, DGA and KS-1™, KS-2™ and KS-3™ series of solvents (Gabrielsen, 2007). The principle of amine scrubbing is represented by the following chemical equations:

CO_2 sorption: $RNH_2 + H_2O + CO_2 \longrightarrow RNH_3^+HCO_3^-$ (under pressure) (2.8)

These solvents can absorb CO_2 at low pressures because they have high reaction energies. This results in high-energy requirements to regenerate the rich solvent. However, energy costs may be reduced if the process can be fully integrated with a power plant where significant amount of low-grade heat may be available. The CH_4 yield and purity in the upgraded gas are both close to 100% (Hagen *et al*., 2001). Chemical absorption is more cost competitive for larger plants than for smaller ones. One advantage of the amine approach is the extremely high selectivity for CO_2 and the greatly reduced volume of the process; one to two orders of magnitude more of CO_2 can be dissolved per unit volume using this process than with water scrubbing. The main problems however, are corrosion, amine breakdown, contaminants buildup, which make it problematic to apply this process to small-scale systems such as dairy farms.

2. 6 Total and Volatile Solids Measurement

One of the most important parameters used in the control decisions in digester slurry is the mixed liquor suspended and volatile solids (VS). Total solid (TS) is the term applied

to the material residue left in a vessel after evaporation of a slurry sample and its subsequent drying in an oven at a defined temperature (either 103 0r 180 ºC). It includes total suspended solids, portion of total solids retained by a filter and total dissolved solids which is the portion that passes the filter. On the other hand, Fixed or VS refers to the residue of total, suspended, or dissolved solids remaining after combustion at 500 ºC. The weight lost during combustion is referred to volatile solids. Analysis of VS in a sample has important applications in that it gives a rough estimate of the amount of organic matter present in the feedstock and degestate of a digester system.

2. 7 Determination of Heating Value of Gaseous Fuel by Gas Calorimeter

The CV of biogas is between 20 – 28 MJ/m^3 depending on the CH_4 content (Cebula, 2009). The heating value of gaseous fuels is determined by means of a gas calorimeter. The calorimeter has a Bunsen type of burner inserted in it which burns the gas under test and the flue gases produced passed through tubes which are surrounded by flowing water. The volume rate of gas flow to the calorimeter is measured by a rotary gas meter. Water conditions are adjusted to cool the products of combustion to the entering air temperature. The rate of water flow through the calorimeter is measured, and its temperature rise is determined too. Neglecting heat exchanger between the calorimeter and its surroundings, the heat received by the water equals the heating value of the fuel. The water, which flows through the calorimeter is collected and weighed. The temperature rise of the water is determined by means of two thermometers. The amount of condensate formed is determined by collecting it in a small container. The pressure of the gas entering the calorimeter is controlled by a regulator. The gas temperature is measured by thermometer and a similar thermometer is used for determining the temperature of the products leaving the calorimeter.

2. 8 Determination of CH_4 Concentrations using Gas Chromatography

The CH_4 content in the biogas usually ranges from 55 – 65% (Bori et al., 2007). In order to upgrade the biogas to natural gas quality, it is essential to determine the specific composition of the farm biogas and its variability. Daniel©Danalyser™ Models 570 is such a Gas Chromatograph (GC) and is capable of calculating heating value, specific gravity and gas sample composition. Figure 2.2 is a schematic representation of this system, showing the basic components of the system, including the injection point, columns, oven, detector and data recorder.

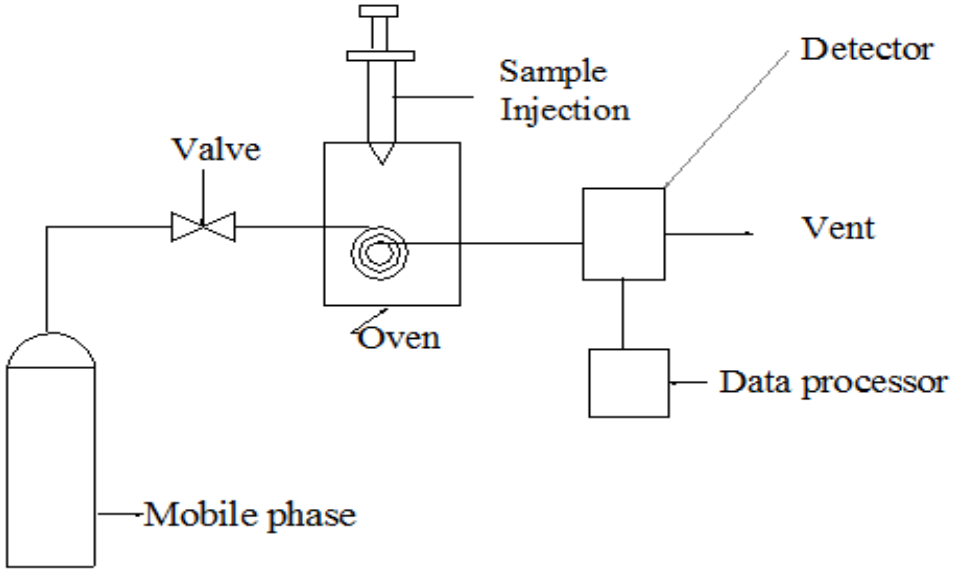


Fig. 2.2 Schematic Diagram of Gas Chromatograph

In general, a GC has an inert carrier gas, such as helium or nitrogen which flows from a large cylinder thorough the injection port, column and detector. The flow rate of the carrier gas is controlled to ensure reproducible retention times and to minimize detector noise. The sample is injected, usually with a syringe, into the heated injection port. In the port, the sample is vaporized and carried into the column, typically a packed or capillary column. In the column, the sample partitions between the stationary and

mobile phases and is separated into individual components based on relative vapor pressures and on relative solubility in the stationary liquid phase. Separation of the different components in the mixture is caused by the varied strength of forces between different components and the stationary phase. The weaker the force between a specific component and the stationary phase is the faster the specific component will elute from the column. The detector signal verses time is represented by a peak. The area of each peak can be integrated and correlated to the amount of the substance that was present in the sample. The size of the peak represents the amount that components that was present in the sample. The peaks correspond to a linear function of the concentration of the corresponding gas.

After leaving the column, the carrier gas and sample pass through the detector. The detector measures the quantity of various components in the sample and generates an electric signal. This signal goes to the data acquisition system, which generates a written record of the analysis, known as a chromatogram. The primary purpose of the inert carrier gas is to transport the sample through the column. It is the mobile phase and does not interact chemically with the sample. The secondary purpose is to provide a suitable matrix for the detector to measure the sample components. Different carrier gases are preferred for various detectors. For example, helium is the most popular carrier gas for the thermal conductivity detector (TCD). The GC is fitted with columns and a thermal couple detector (TCD) detector that can detect various biogas components. Due to the increasing interest in biogas, there is a growing demand for fast and efficient analysis technology and 490 Micro GC is among the new generation technology. It has two channels, one configured with a CP-Molsieve column to separate and analyze H_2, O_2, N_2, CH_4 and CO_2, and the other is equipped with a CP-PoraPLOT U column, to analyze CO_2 and H_2S.

2. 9 Standard curve for Gas Chromatography

Calibration curves show the relationship between chromatogram peak intensity and compound concentration. The calibration curve for the GC is important in establishing the order and also monitoring the composition of the gases under test. To determine the composition, calibration curves have to be made the same using the similar conditions. This is done using known amounts of the gas needed to be analysed.

CHAPTER THREE

3.0 METHODOLOGY

3. 1 Experimental Design

The prerequisite to the construction of the biogas purification system involved a number of processes. The research first investigated the influence of the feedstock taken by the animals on the composition of the biogas. Samples of the slurry from three digesters were collected and analyzed for the TS and VS.

3.2 AD Systems nfluent and effluent sampling and analysis

3.2.1 Location of the AD systems

The study analyzed the performance of AD cow dung systems of three farms in Ongata Rongai, division in Kajiado County about 20 Km west of Nairobi. The three digester systems had a holding capacity of 4 m^3, 6 m^3 and 12 m^3 respectively. Plate 3.1 shows the features of one of the fixed dome digester. The animal feed giving rise to the dung feed stock was varied but comprised of napier grass, weed, dry maize stock, grass and Lucerne. The resulting gas produced was utilized for cooking and lighting. The influent was made up of raw manure slurry entering the digester from the mixing chamber while the effluent exited the digester through the expansion chamber.

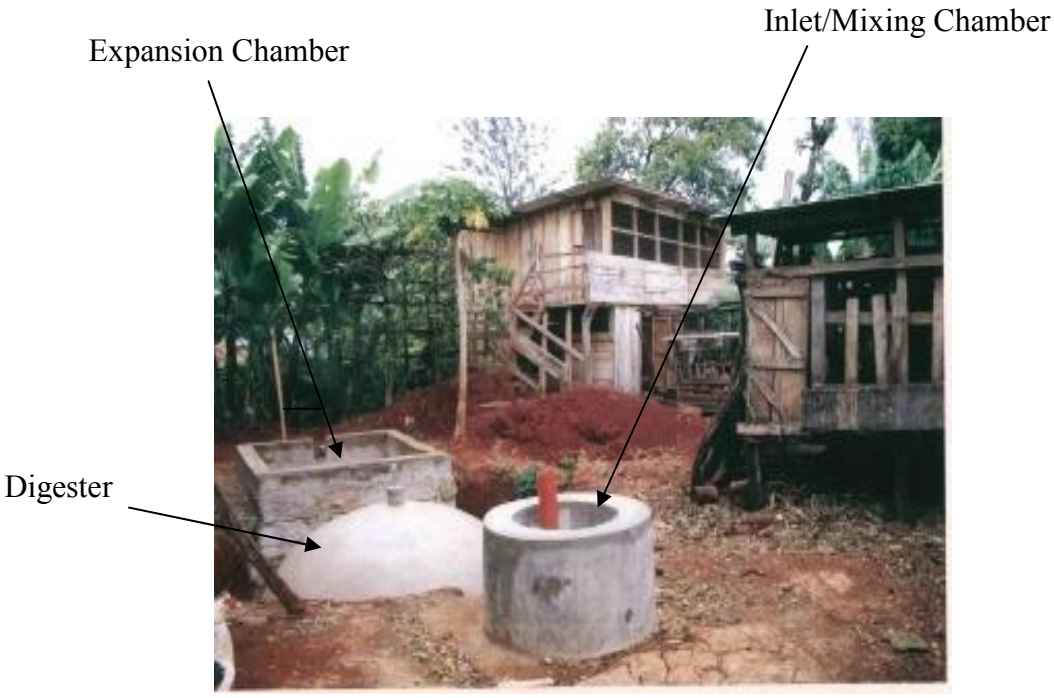


Plate 3.1: Fixed Dome Biogas Plant

3.2.2 Determination of Total Solids

The analysis of the Total Solids (TS) was performed as stipulated in the Standard methods for analysis of water (APHA, 2005). This was to determine the TS content which is the sample residue left in a crucible after evaporation of the digesters samples. Plate 3.2 shows the samples taken for both influent and effluent. Each sample from the feedstock and digestate was a composite sample of a 100 gm.

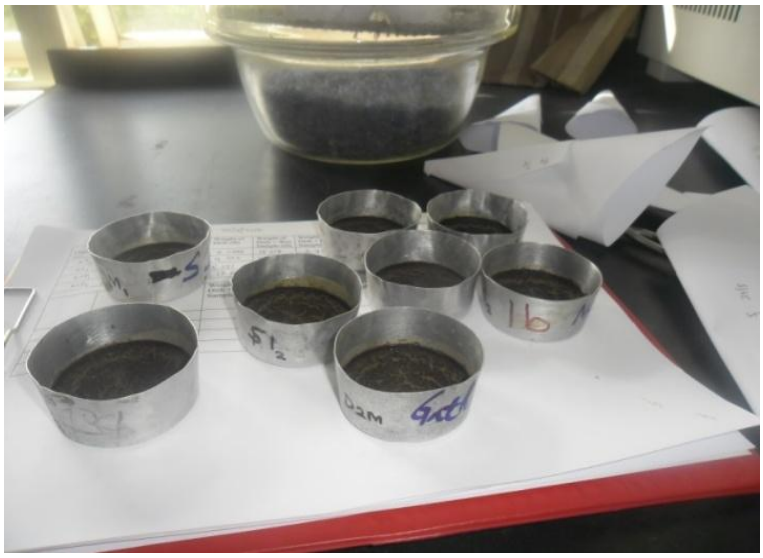


Plate 3.2: Samples of Influent and Effluent

The sample of the influent and digestate was evaporated in a weighed dish and dried to constant weight in a convection oven for 3 hours at a temperature of 105 °C. The samples from the oven were then placed in a desiccator to remove all the moisture before the final measurement.

The equipment and apparatus for the TS test included: -

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

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

$$TS = \frac{(A-B)}{(D-B)} \text{ x } 100\% \qquad (3.1)$$

Where A = weight of dish + dry sample

B = weight of dish

D = weight of dish + wet sample

3.2.3 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. Plate 3.3 shows the inorganic ashes in the crucibles.

Plate 3.3: Inorganic Ashes in Crucibles

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. The VS% was calculated using equation 3.2.

$$VS = \frac{(A-C)}{(A-B)} \text{ x } 100\% \qquad (3.2)$$

Where A = weight of dish + dry sample

B = weight of dish

C = weight of dish + sample after ashing

3.3 Determination of CH_4, CO_2, N_2 and O_2

The Gas Chromatograph, GC-8A (Shimadzu) in the Food Science Laboratory at JKUAT was used to perform the biogas chromatography in the sample raw gas. The main components of the GC included: carrier gas, flow controls, sample inlet and sampling devices, columns, controlled temperature zone or ovens, detectors and data acquisition systems.

The GC was equipped with a thermal conductivity detector (TCD) and measured the difference in the thermal conductivity of each of the compound in the biogas. The carrier gas used in this application was helium. The output stream of the carrier gas was regulated at 2 bar pressure into the GC. In order to detect CH_4 and CO_2 gases the GC was calibrated with 99.999% standard of the two gases at the start of the study.

The biogas stream for GC analysis was supplied from the digester plants using plastic storage bags. A sample containing 0.2 ml of this gas was sucked from the bags using a syringe and injected into the GC. The separated components were recorded as peaks on the data processor. The operating parameters used for the GC-8A are given in Table 3.1

Table 3.1 GC Operating Parameters

Parameter	Value
Detector temperature	150°C
Oven temperature	150°C
Carrier gas	Helium
Carrier gas pressure	2.2kg/cm^2
TCD amplifier	100mA
Column type	Stainless steel/Porapak porous polymer
Column length	3m or 10ft

3.4 Titrimetric Determination of Hydrogen Sulphide

The GC 8A did not have the capacity to determine percentage composition of H_2S and thus a different method was adopted for this gas. The technique used for the determination of the H_2S gas in the biogas was by wet chemical titration method. The following apparatus and reagents were used:-

i. Gas flask
ii. Rotary vacuum pump
iii. Mercuric acetate ($\alpha(CH_3COO)_2Hg$)
iv. Sodium hydroxide (NaOH)
v. Acetone
vi. Dithizone indicator
vii. 2 ml and 5 ml pipette
viii. Pipette filler

A concentrated solution of 25% NaOH was first prepared and then put in the gas flask. The gas flask was thoroughly evacuated to get rid of all atmospheric contamination. A sample containing 10 ml of biogas was then injected into this glass flask containing 25%

NaOH solution and shaken vigorously to dissolve the H_2S. To this mixture, 5 ml of acetone and a drop of dithizone indicator were added. The resultant was then titrated with a solution of 0.01M mercuric acetate and the end point was determined when the color changed from yellow to pink. This was done in triplicate and resulting volumes of the consumed mercuric acetate was recorded from which the concentration of H_2S was evaluated.

% H_2S = Titre volume of $\alpha(CH_3COO)_2Hg$ x concentration of $\alpha(CH_3COO)_2Hg$ x relative Molecular mass of H_2S x 1000 / volume of sample taken. (3.3)

Data:

Relative molecular weight H_2S = 34 grams

Volume of sample taken = 5 ml

Concentration of $\alpha(CH_3COO)_2Hg$ = 0.001 molar

3.5 Removal of H_2S, CO_2 and H_2O

Biogas from the three digesters was fed into a set of reactor columns which were packed with materials to adsorb H_2S, CO_2 and H_2O respectively. The unit consists of four gas tight PVC containers connected with plastic hose pipes as illustrated in Figure 3.1. The system incorporated a flow meter, packed column, packing materials, outlet measuring points and control valves.

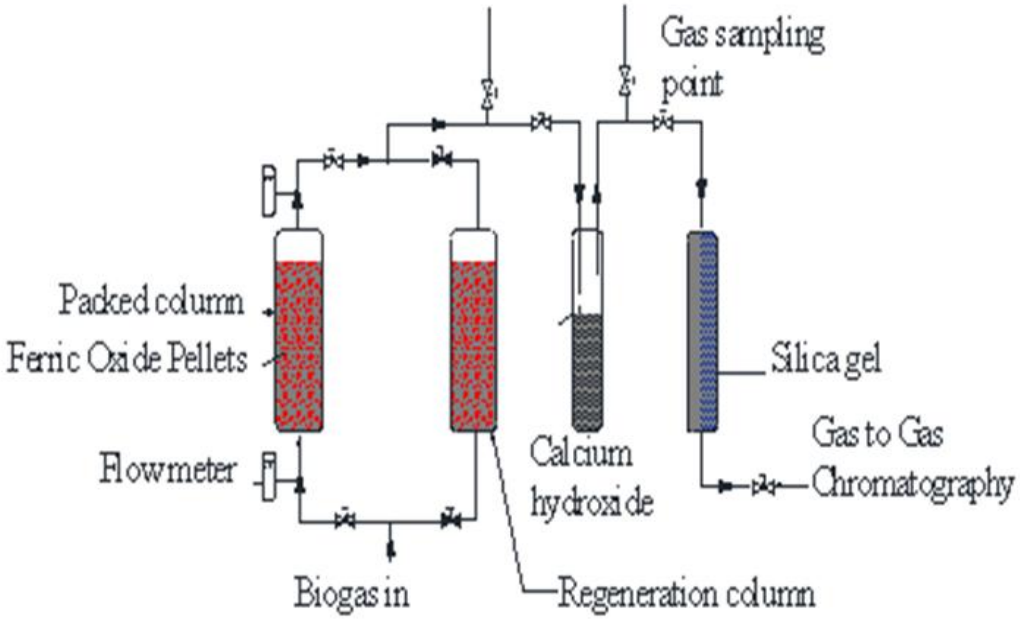


Fig. 3.1 A Schematic Diagram Reactor Column

The first two columns containing ferric oxide pellets had a height of 150 mm and diameter of 75 mm and are closed on both ends. One of the two columns was operational while the other one was utilized for regeneration of ferric oxide The other two columns containing calcium hydroxide solution and silica gel respectively had a height of 150 mm and a diameter of 50 mm. On the top covers of each column, holes of 10 mm to support pipe nipples were drilled onto which hoses were fitted to allow the flow of the gas. After construction the columns were filled with respective adsorption materials. PVC materials were chosen because they are cheap and are not affected by exposure to the biogas components. The designs considerations were that the materials used were locally sourced and there was to be no energy requirements for the system operation.

3.5.1 Preparation of Ferric Oxide

Ferric oxide was prepared from machine chippings obtained from the Mechanical engineering workshop of JKUAT. They were wastes from the machined process of mild steel. Plate 3.4 shows the workshop machine process of mild steel.

Plate 3.4: Workshop Machine Chippings

The chippings were treated with a dilute solution of vinegar and the resultant exposed in air to allow the oxidation process (rusting) of the iron as shown in Equation 3.4.

$$2Fe_{(s)} + 2CH_3CO_2H_{(aq)} \longrightarrow Fe_2O_{3(s)} + 3H_{2(g)} + 4CO_{2(g)} \quad (3.4)$$

3.5.2 Hydrogen Sulphide Removal Unit

Experiments of H_2S removal by the materials were performed in this column. The unit comprised of two vertical columns packed with 1 kg of ferric oxide pellets in which experiments for the removal of H_2S were performed. The biogas with the various constituents was introduced in the removal unit through a PVC flexible pipe. The biogas was passed through the bed of ferric oxide pellets. The gas flowed from the bottom of the first column, then through the ferric oxide bed and finally exited on the

top of the column with H_2S being stripped off from the gas stream.

The ferric sulphide was deposited at the surface of the adsorbent material. The H_2S adsorption from the sampled gas was studied against the variable contact time of the gas in the column. The system was tested for various contact time intervals ranging from 5 minutes to 50 minutes to determine the concentration decrease in H_2S. Constant flow rate of the gas was introduced for the range of 15 –20 litres/min.

3.5.3 Carbon Dioxide Removal Unit

The unit comprised of a vertical column that was filled up with an alkali namely Calcium Oxide solution. The source of calcium oxide was from limestone rocks that were obtained locally. The limestone rocks were first crushed to powder and then this powder first heated in a furnace for an hour at a temperature of 1000 °C to release off CO_2 gas resulting to calcium oxide (CaO) .

In this column the CO_2 was absorbed and transferred into the aqueous molar solution of hydroxide. A concentration of 15% calcium hydroxide $(CaOH)_2$ was then prepared from the CaO and poured into the second column. The biogas leaving the first column was supplied from the top through a perforated pipe and dipped into the solution bubbling through it for proper mixing. As CH_4 is a passive odorless gas which does not react with any of the packing materials in the scrubbing columns, it was diverted to the upper part of the column with its quality increased.

3.5.4 Moisture Removal Unit

The removal unit comprised of a transparent column packed with 150 gm anhydrous silica gel (Mesh 4 – 6 mm) mixed with cobalt chloride indicator. As expected the biogas

is produced in a hydrated environment and as such moisture will be a part of product. Moisture was removed by passing the biogas through the column and all the water was removed by the anhydrous silica gel. The exhaustion of the packing material was indicative by the colour change of cobalt chloride from blue to pink. Plate 3.5 shows the packing material before it was exhausted.

Plate 3.5 Silica Gel Blue Self Indicating

The effect of contact time on the removal of moisture was investigated by varying the contact time to between 5 – 50 minutes. This was achieved by regulating the biogas flow rate to a range of 15 – 20 litres/minute. The quantity of the removed moisture was determined gravimetrically. This was done by recording the mass of silica gel before and after the removal process. The difference gave the quantity of water removed.

The quality of the biogas was analysed before and after removal of the contaminants to ascertain the quality of the biogas.

3.6 Biogas Energy Testing

In this study, due to unavailability of a gas calorimeter, the CV and consequently the efficiency of the purified biogas was determined by measuring and recording the boiling time taken by water that was subjected to heating. The CV of the resulting gas is dependent on the concentrations of CH_4 and CO_2. The raw biogas from each of the three

digesters and the purified gas from the reactor were compared through a water heating test to establish the improvement of the heating value. The test setup used on the three digester systems is as illustrated in Figure 3.2. In order to compare the impact of purification on the CV and heating time, both raw and purified biogas were used to boil 500 ml of water for a specified time. Water in an open vessel gained energy from the burning biogas fuel and the value of energy gained is equivalent to energy gained to raise the temperature of the water to boiling point. Five samples of similar condition of this test with raw and purified gas were repeated to determine the relative purity of the gas and the results are as discussed in section 4.6.

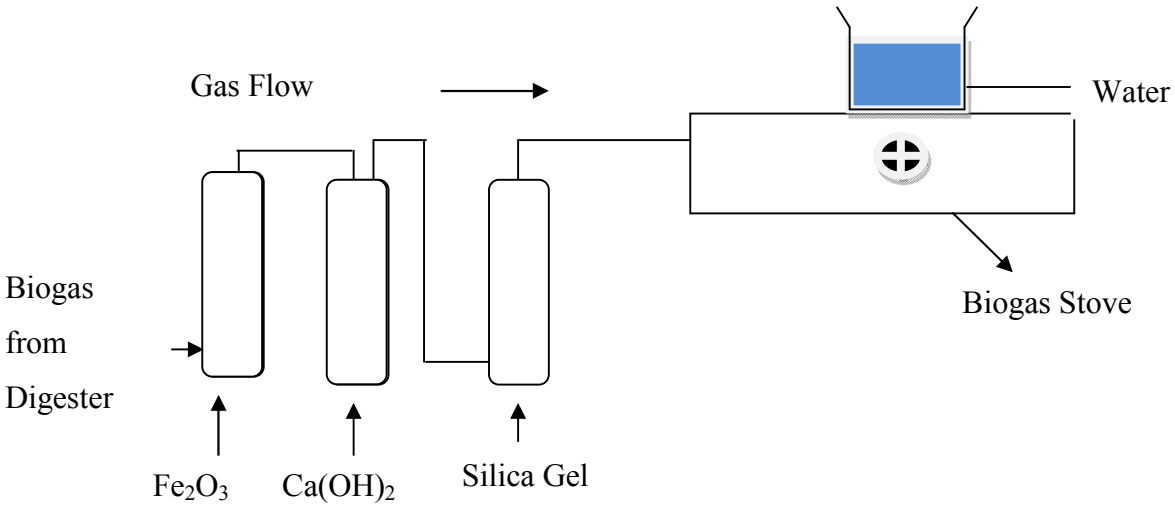


Fig. 3.2 Setup for Determining Heating Value of Biogas

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Total Solids and Volatile Matter Content

Analysis of the content of total solids and volatile matter for the various days were recorded as shown in Tables 4.1A, 4.1B and 4.1C.

The results show that VS content in each case decreased due to the bio-degradation of organic material to produce CH_4 and CO_2.

Table 4.1A TS and VS Destruction Results: Digester 1

DAY	% TOTAL SOLIDS of SAMPLE			% VOLATILE SOLIDS	
	INFLUENT	EFFLUENT	% CHANGE	INFLUENT	EFFLUENT
1	8.39 ± 0.15	7.10 ± 0.21	15.38 ±0.28	84.00 ± 2.13	72.70 ± 2.89
2	8.99 ± 0.16	7.30 ± 0.20	18.80 ± 0.18	81.00 ± 2.85	75.60 ± 2.69
3	8.46 ± 0.15	7.17 ±0.25	15.25 ± 0.20	74.50± 2.25	70.00 ± 3.10
4	8.69 ± 0.36	7.20 ± 0.14	17.15 ± 0.25	82.50 ± 2.12	74.15 ± 2.05
5	11.70 ±1.15	8.33 ± 0.35	28.80 ± 0.75	82.40 ± 3.14	73.70 ± 2.01
6	8.12 ± 0.13	6.47 ± 0.23	20.32 ± 0.18	80.90± 2.89	73.70 ± 2.45
7	8.76 ± 0.17	7.79 ± 0.14	11.07± 0.21	80.18 ± 2.46	78.20 ± 3.24
8	8.16 ± 0.15	6.73 ± 0.11	17.52 ± 0.13	82.40 ± 2.13	77.91± 2.89
AVERAGE	**8.91± 0.17**	**7.26 ± 0.20**	**18.04 ±0.27**	**81.00 ± 2.50**	**74.50 ± 2.67**

Table 4.1B TS and VS Destruction Results: Digester 2

DAY	% TOTAL SOLIDS of SAMPLE			% VOLATILE SOLIDS	
	INFLUENT	EFFLUENT	% CHANGE	INFLUENT	EFFLUENT
1	9.53± 1.31	9.02± 1.21	5.35± 1.26	81.50± 2.30	81.60± 1.29
2	9.73± 1.32	9.30± 1.01	4.42± 1.17	85.10± 2.30	80.50± 1.18
3	9.64± 1.21	9.58± 0.17	0.62± 0.69	87.00± 2.30	76.00± 1.27
4	9.63± 1.41	9.16± 0.19	4.88± 0.80	83.30± 2.55	81.05± 0.78
5	9.55± 1.67	7.53± 0.87	21.15± 1.27	83.10± 2.87	80.00± 1.28
6	9.98± 1.52	9.15± 1.42	8.32± 1.47	82.30± 2.62	79.50± 1.43
7	9.33± 1.42	8.19± 0.97	12.22±1.20	86.35± 2.63	79.50± 1.01
8	9.48± 1.36	8.36± 0.98	11.31± 1.17	92.18± 3.11	85.43± 1.23
AVERAGE	**9.61± 1.40**	**8.79± 0.85**	**8.60± 1.13**	**85.10± 2.59**	**80.45± 1.18**

Table 4.1C TS and VS Destruction Results: Digester 3

DAY	% TOTAL SOLIDS of SAMPLE			% VOLATILE SOLIDS	
	INFLUENT	EFFLUENT	% CHANGE	INFLUENT	EFFLUENT
1	8.76± 1.67	7.49±1.17	14.50±1.42	86.74± 2.80	70.80± 1.21
2	7.63± 1.56	7.41± 1.23	2.88± 1.40	92.60± 3.20	72.00± 1.43
3	8.89± 1.21	8.38± 1.18	5.74± 1.20	83.13± 2.70	71.90± 1.38
4	9.71± 1.43	7.45± 1.53	23.27± 1.48	75.50± 3.80	70.60± 1.41
5	9.20± 1.37	7.23± 1.27	21.41±1.32	74.60± 2.50	70.30± 1.31
6	7.57± 1.52	7.41± 1.28	2.11± 1.40	78.75± 2.78	75.64± 1.42
7	7.64± 1.21	7.38± 1.19	3.40± 1.20	75.97± 3.10	71.10± 1.36
AVERAGE	**8.49± 1.43**	**7.54± 1.27**	**11.20± 1.35**	**81.04± 2.98**	**71.76± 1.20**

The TS decreased in the digesters by variable percentages in the ranges of 8.91 to 7.26, 9.61 to 8.79 and 8.49 to 7.54 with respect to feedstock in digester 1, 2 and 3. The digester where the animals were fed with dry feedstock show much higher TS content than those fed with fresh ones. The VS is higher in the fresh feedstock samples than in the dry one. It can be deduced that the fresher the plant material is, the higher the VS content. However if the TS is lower, a greater mass of plant material must be added to the digester in order to achieve the same amount of VS. If the value becomes an issue due to the fact that the density of the plant material is much than that of water or manure then it is appropriate that the plant materials be dried before being added to the digester.

4.2 Results of the GC

4.2.1 CH_4 and CO_2 Analysis Using Gas Standards

Linear calibration curves for CH_4 and CO_2 are plotted in Figures 4.1 and 4.2 respectively. Injection of **CH_4 (99.99%)** and **CO_2 (99.99%)** gas standards was conducted to determine the precision of the two gases. The amounts injected in the GC with pure CH_4 and CO_2 were 20 µl, 40 µl, 60 µl, 80 µl and 100 µl.

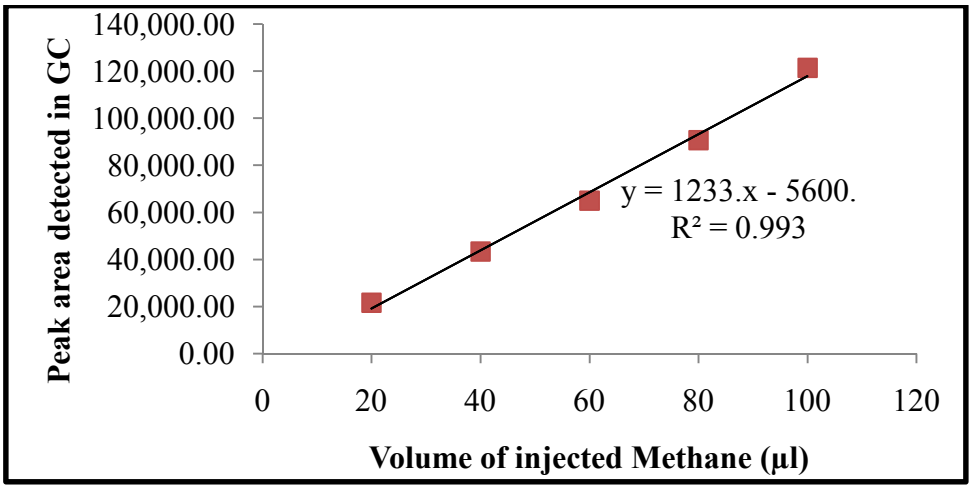


Fig. 4.1 Calibration Curve for Methane detection in the GC

Table 4.2 Regression Statistics for CH_4

Multiple R	0.992116
R^2	0.9934294
Adjusted R^2	0.98
Standard Error	4.57617
Observations	5

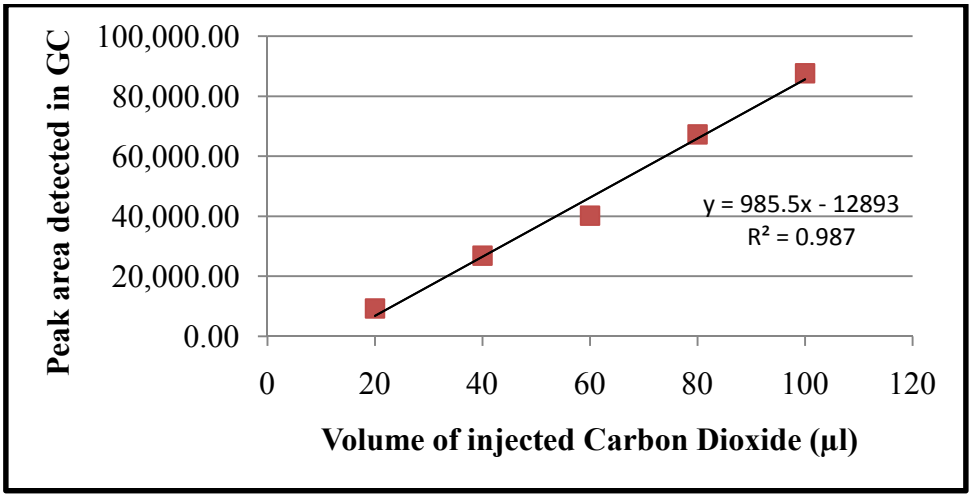


Fig. 4.2 Calibration Curve for Carbon Dioxide detection in the GC

Table 4.3 Regression Statistics for CO_2

Multiple R	0.993832
R^2	0.987702
Adjusted R^2	0.983603
Standard Error	4.049325594
Observations	5

The large R^2 values that is greater than 0.98 indicated a very high correlation between the gas concentration and the peak area.

4.3 Composition of Raw Biogas

Although not the only components analyzed, there were four readings of significance gathered from the GC namely, CH_4, CO_2, N_2 and O_2. The species eluted in the following order N_2, CH_4, CO_2 and O_2. The results were printed directly to a recorder attached to the GC.

Figure 4.3 shows a chromatogram of one of the digester gas sample that was analysed on the GC-8A. The figure demonstrated a four peak group during a retention time of 5 minutes. The four peak group was observed at average 0.67, 1.033, 1.387 and 4.338 minutes representing N_2, CH_4, CO_2 and O_2 respectively.

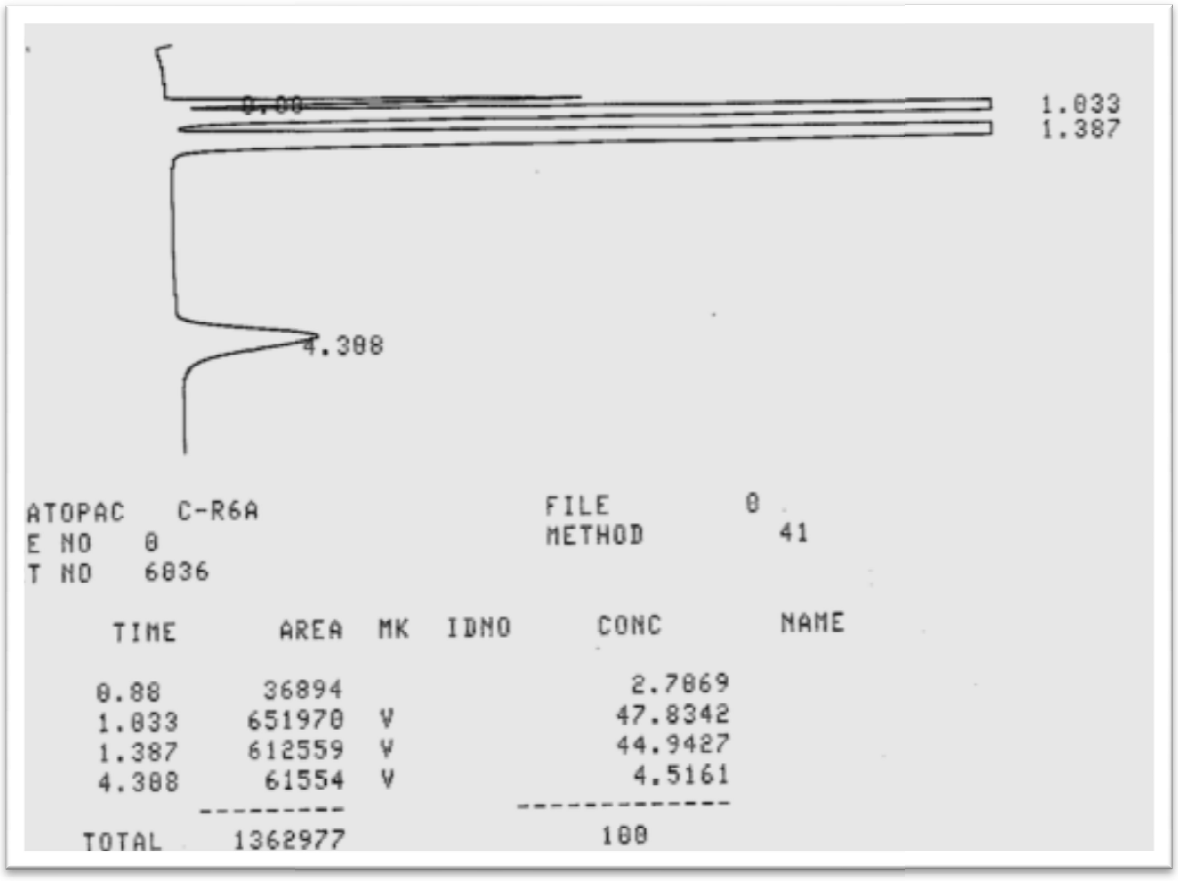


Fig. 4.3 Chromatogram from the GC-8A 0.2 ml injection of the Biogas

The final biogas chemical composition in terms of CH_4, CO_2 and N_2 contents for the three digesters during the duration 18th April and 6th June 2012 is as shown in Tables 4.4A, 4.4B and 4.4C as analyzed from the GC.

Table 4.4A Biogas Concentration for Digester 1

DAY	CH_4 %	CO_2 %	N_2 %
1	50.7± 0.57	36.9± 0.31	7.2± 0.12
2	49.8± 0.52	36.2± 0.27	6.5± 0.23
3	56.8± 0.47	25.5± 0.27	12.8± 0.11
4	49.6±0.32	36.1± 0.45	7.0± 0.14
5	44.4± 0.68	46.0± 0.37	4.4± 0.15
6	46.1± 0.63	44.8± 0.44	4.5± 1.35
7	48.6± 0.46	43.0± 0.3	2.9± 0.3
8	48.5± 0.5	42.8± 0.47	4.3± 1.20
AVERAGE	**49.3± 0.5**	**38.9± 0.45**	**6.2± 0.45**

Table 4.4B Biogas Concentration for Digester 2

DAY	CH_4 %	CO_2 %	N_2 %
1	54.5± 0.36	36.2± 0.33	4.6± 0.15
2	53.3± 0.24	35.5± 0.37	4.8± 0.12
3	47.5± 0.43	43.0± 0.28	4.0± 0.20
4	49.3± 0.28	44.7± 0.25	2.8± 2.21
5	43.4± 0.54	47.0± 0.39	3.0± 1.32
6	44.5± 0.67	48.3± 0.38	2.9± 1.72
7	46.4± 0.48	46.6± 0.34	2.5± 1.82
8	46.1± 0.45	46.4± 0.33	2.4± 2.10
AVERAGE	**48.1± 0.43**	**43.5± 0.33**	**3.48± 1.21**

Table 4.4C Biogas Concentration for Digester 3

DAY	CH_4 %	CO_2 %	N_2 %
1	44.2± 0.43	45.7± 0.32	3.9± 0.15
2	48.9± 0.41	42.8± 0.39	3.1± 0.21
3	49.8± 0.39	43.5± 0.28	3.2± 0.24
4	46.7± 0.35	45.1± 0.27	2.6± 0.39
5	47.9± 0.38	46.2± 0.33	2.4± 0.14
6	47.8± 0.34	44.9± 0.28	2.7± 0.17
7	47.1± 0.31	44.3± 0.29	2.6± 0.21
AVERAGE	**47.5± 0.37**	**44.6± 0.31**	**2.9± 0.22**

From the results, the CH_4 production rate varied from 43.4% to 54.5% based on the type of feedstock. The highest values of the CH_4 were 54.5%, 50.7% and 49.8% for digester 1, 2 and 3 respectively. On the other hand, the average values of CH_4 were 49.3%, 48.1% and 47.5% respectively while those of CO_2 were 38.9%, 43.5% and 44.6% for the three digesters.

These results show that there is not much difference between the digesters regarding the CH_4 and CO_2 content. However the difference in the feedstock explains that the materials which are more easily degradable breaks fast in comparison with complex materials and this being the reason for the slight variations of the composition percentages. The findings also showed that the comparisons of CH_4 yields reported in the introduction cannot be precise because of possible differences in the feedstock and the experimental conditions.

The data obtained from the GC analysis in terms of the composition agreed with the literature review although the concentration of the CH_4 is low while that of CO_2 is high.

The higher levels of CO_2 which is also the main contaminant are indicative of poor CH_4 content and therefore a lower energy value.

Table 4.5 show a summary of the H_2S concentration titrimetry results for the sampling period.

Table 4.5 % H_2S Concentration of Raw Gas

DAY	Digester 1 (%)	Digester 2 (%)	Digester 3 (%)
1	0.00531±0.03	0.00142± 0.12	0.00280± 0.01
2	0.00528± 0.03	0.00129± 0.14	0.00232± 0.19
3	0.00574± 0.02	0.00130± 0.14	0.00299± 0.21
4	0.00523± 0.12	0.00145± 0.21	0.00271± 0.21
5	0.00524± 0.12	0.00124± 0.22	0.00233± 0.17
6	0.00538± 0.01	0.00145± 0.23	0.00251± 0.18
7	0.00545± 0.01	0.00138± 0.14	0.00267± 0.15
8	0.00589± 0.02	0.00135± 0.22	0.00343± 0.01
AVERAGE	**0.00544± 0.04**	**0.00136± 0.18**	**0.00272± 0.14**

The H_2S concentration was also found to be within the range in the literature review although with some variations amongst the three digesters. This is still probably because of the different feedstock as early discussed.

4.4 Hydrogen Sulphide Adsorption

Hydrogen Sulphide was scrubbed using ferric oxide pellets packed in a column. This adsorbent material was prepared and subsequently analysed.

4.4.1 Elemental Analysis of the Ferric Oxide

The elemental composition of the pounded ferric oxide was carried out and the results presented as shown in Table 4.6.

Table 4.6: Elemental composition of Ferric Oxide

Sio_2	Al_2O_3	Cao	MgO	Na_2O	K_2O	TiO_2	MnO	Fe_2O_3	Loss on ignition
2.83	0.21	0.17	0.15	0.96	0.004	0.03	0.40	78.6	16.23

The results show that the there was a high amount of ferric oxide and some other small quantities of the indicated metals.

4.4.2 Ferric Oxide Pellets

The ferric oxide was moulded into pellets. Different sizes of pellets were tried out until an appropriate size was attained that ensured maximum contact surface. Plate 4.1 shows a presentation of a 4 mm diameter product obtained.

Plate 4.1: Ferric Oxide Pellets

The composition of the adsorbent material in the pellets was a combination of ferric oxide and calcium oxide which served as a binder as this was realized to increase the absorption rate. The ferric adsorbent material was made in this matrix to increase the surface area of contact of the biogas and the adsorption material. The resulting material was non-hazardous, easy to dispose off and could be regenerated after adsorption of the sulphide.

4.4.3 Performance of the H_2S Adsorption Column

The results obtained for the performance of the hydrogen sulphide adsorption column before and after purification of the biogas were presented graphically in Figure 4.4.

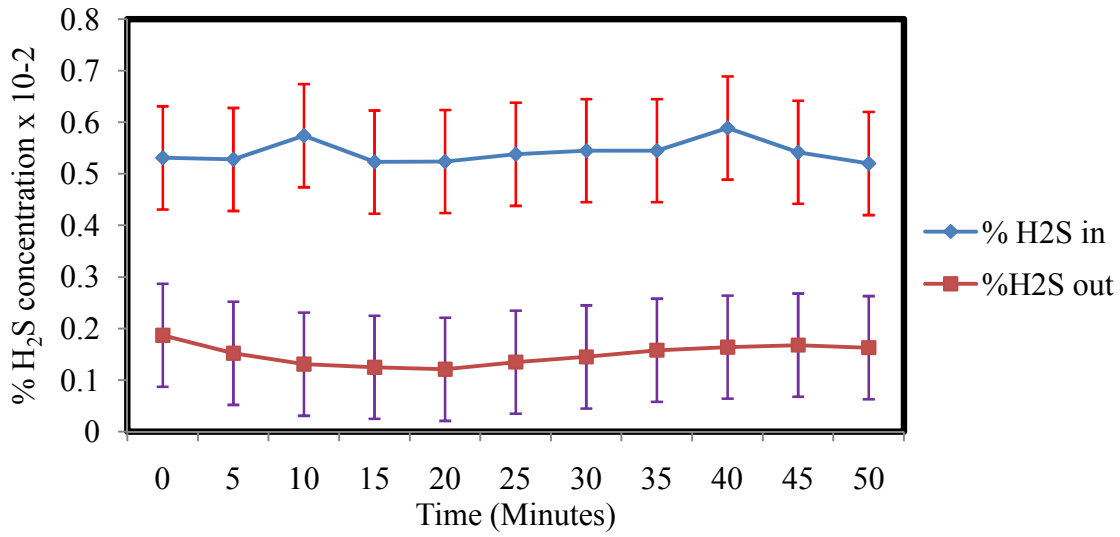


Fig. 4.4 Comparison of H_2S Concentration after Purification

The level of the H_2S reduced in the biogas by passing the biogas through the adsorption material. The material converted H_2S to Iron sulphide. The chemical reaction that took place between the H_2S and Ferric oxide is as shown in equation 4.1.

$$2Fe_2O_{3(s)} + 6H_2S_{(g)} \longrightarrow 2Fe_2S_{3\,(s)} + 6H_2O_{(l)} \qquad (4.1)$$

The results of H_2S adsorption by ferric oxide showed that the best operating time was 20 minutes with a reduction of about 80%. When the H_2S concentration in the biogas was increased, the efficiency of H_2S removal was decreased. The ferric oxide is consequently effective in removing the H_2S present in the biogas.

4.5 CO_2 Measurements

The variation with time of the CH_4 concentration during the purification process is shown in Figure 4.5. The plot is as a result of the CO_2 in the biogas being absorbed by the $Ca(OH)_2$ solution. The alkali guaranteed CO_2 reaction in the biogas intensively through an acid-base neutralization reaction absorbing and reducing the targeted gas. The moles in this strong base solution were in excess in comparison to those in the gas and therefore CO_2 was dissolved. The CO_2 absorption chemical reaction is shown in equation 4.2, 4.3 and 4.4.

$$CO_{2\,(g)} + H_2O_{\,(l)} \longrightarrow H_2CO_{3\,(aq)} \quad (4.2)$$

$$CaO_{\,(s)} + H_2CO_{3(aq)} \longrightarrow CaCO_{3\,(s)} + H_2O_{(l)} \quad (4.3)$$

$$Ca(OH)_{2\,(aq)} + H_2CO_{3\,(aq)} \longrightarrow CaCO_{3\,(s)} + H_2O_{\,(l)} \quad (4.4)$$

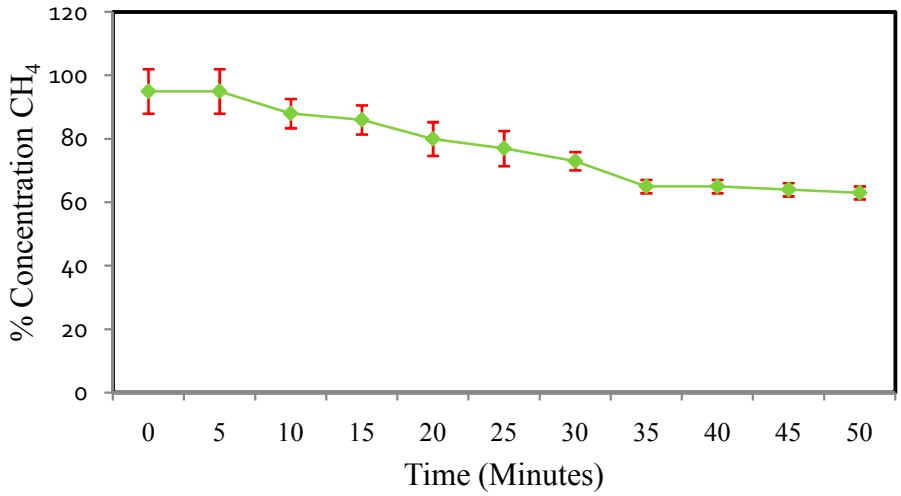


Fig.4.5 Comparison of CH_4 Concentration after Cleaning

From the graph, it can be seen that the CH_4 concentration at the beginning was as high as 95% as a result of CO_2 being absorbed at a faster bubbling rate. The results show that the reactor removed CO_2 resulting in CH_4 being enriched in the biogas. However this was only maintained only for a short time after the solution was saturated with the absorbed CO_2. To curb this decline required a maintenance of the initial conditions for the aqueous solution of $Ca(OH)_2$. Figure 4.6 on the other hand shows the removal rate of CO_2 from biogas for various contact timings when it reacted with the solution. At the beginning the absorbent rate is high giving the CH_4 concentration of about 95% but decreases with time as the absorbent precipitates. The almost linear relationship was obtained within the different range of operating times of the $Ca(OH)_2$ solution.

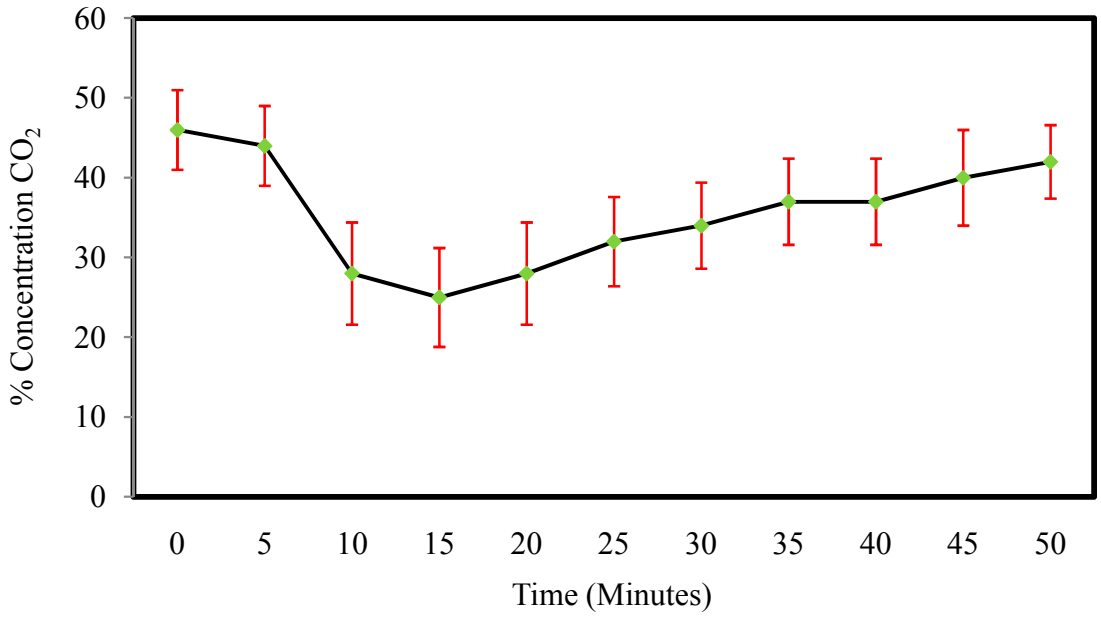


Fig. 4.6 Comparison of CO_2 Concentration after Upgrading

The graph shows the variations of CO_2 against time as the biogas is passed through the $Ca(OH)_2$ column. As shown, the CO_2 concentration decreased from 46% to 25% in the first 15 minutes. After sometime the CO_2 increased to 42%. An average of 10% removal in CO_2 was noted during the test. The relatively fast saturation time is an indication that the percentage CO_2 is very high and to maintain high adsorption rate a

substantial fraction of the original volume of the solution needed to be replaced or regenerated. The $CaCO_3$ precipitate which is a product of CaO was regenerated by heating the solution to a temperature of about 600 °C.

$$CaCO_{3\,(s)} \longrightarrow CaO_{\,(s)} + CO_{2\,(g)} \qquad (4.5)$$

This dissociated back to CaO and CO_2 as shown in equation 4.5.

4.6 Removal of Water Using Silica Gel

Results for the silica gel tests are as presented in Table 4.7. As the beads started taking up moisture, they gradually turned in to pink colour. After 10 minutes a light blue color change in the indicator gel was observed near the bottom of the column. This was a sign of initial point of saturation in the column.

Table 4.7 Data for Silica Gel Test

Time (Minutes)	Weight (grams)
5	150.0 ± 1.50
10	150.3 ± 0.80
15	150.7 ± 0.50
20	150.9 ± 1.00
25	155.2 ± 0.17
30	161.0 ± 0.13
35	167.0 ± 0.19
40	172.0 ± 1.20
50	175.0 ± 0.90

The silica gel was then weighed over the other intervals as the indicating gel slowly turned into pink color. Qualitative method was used in the determination of the moisture present.

From observation in figure 4.7, the weight of the silica gel remained the same within the first 10 minutes but after this point the weight started to increase.

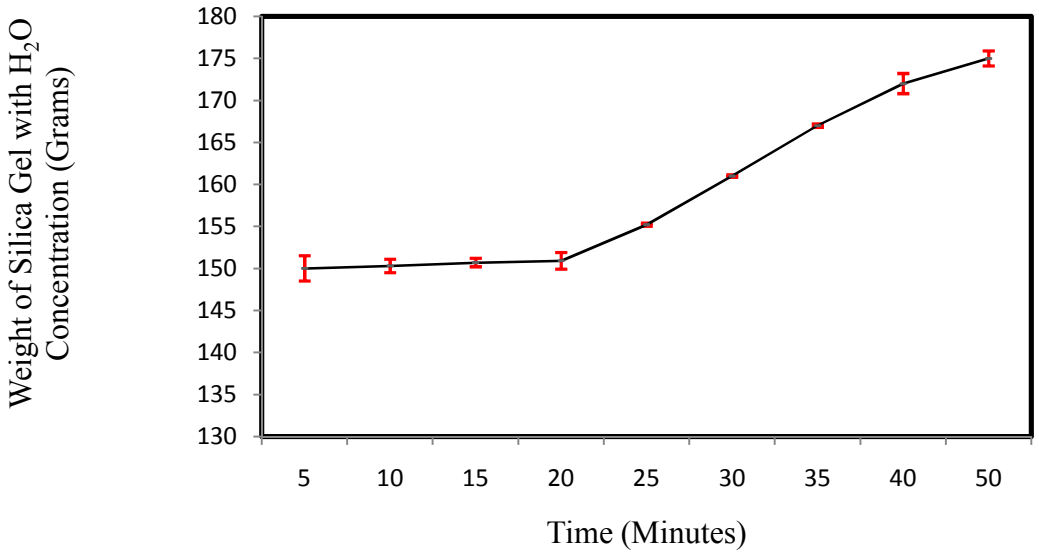


Fig. 4.7 Results for the Silica Gel Tests

According to the obtained data it was found the silica gel effectively removed the water. Silica gel has an ability to be reused in the removal of H_2O. It was reactivated by heating it in an oven at 150 °C for 3 hours to remove the collected H_2O. The indicating silica gel then returned to blue color after being regenerated.

4.6 Heating Value

The quality of the biogas was monitored by determining the time taken for that fuel to boil 500 ml of water. This was done by maintaining all other parameters at their optimal values. The results of the average water boiling time and efficiency as a function of experimental variables before and after purification of biogas is as depicted in Table 4.8.

Table 4.8 Average Time before and after Purification

DAY	Time before and after purification (min) Digester 1		ɳ %	Time before and after purification (min) Digester 2		ɳ %	Time before and after purification (min) Digester 3		ɳ %
1	7.8	2.7	65	7.6	2.5	67	8.1	2.7	67
2	7.9	2.75	65	7.8	2.6	67	7.8	2.6	67
3	7.5	2.4	68	7.6	2.7	64	7.9	2.7	66
4	7.6	2.5	67	7.3	2.8	62	7.6	2.7	64
5	7.5	2.3	69	7.5	2.4	68	7.7	2.7	65
AVERAGE	7.7	2.5	67	7.6	2.6	66	7.8	2.7	66

The results obtained were graphically presented as shown in Figure 4.8

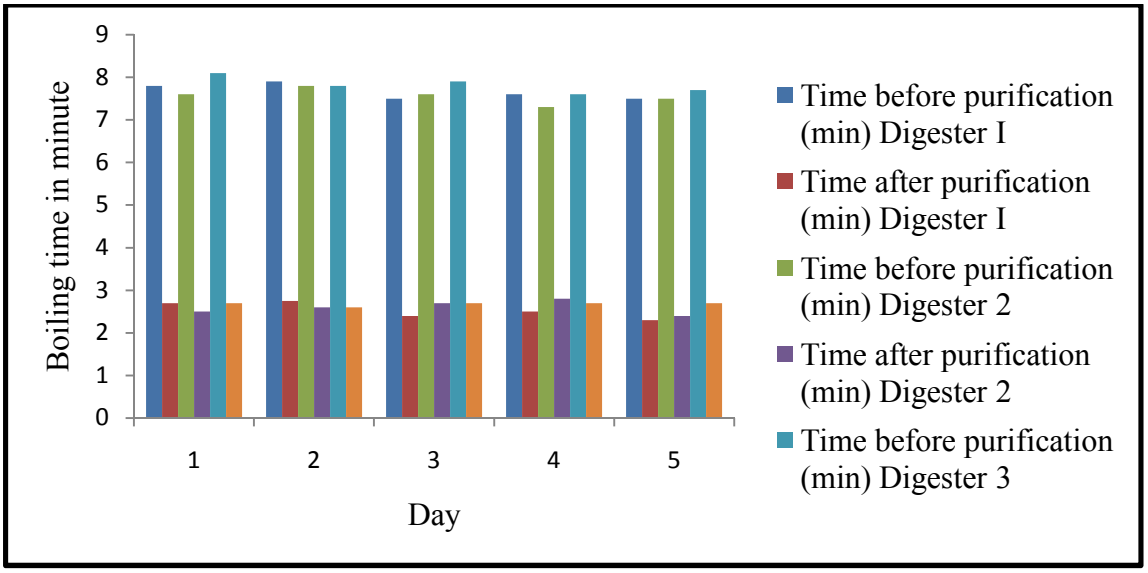


Fig. 4.8 Water Boiling Time before and after Purification

It was observed that the average time required for heating to boil 500 ml of water with raw gas varied between 7.6 and 7.8 minutes while using the purified gas brought the time to between 2.5 and 2.7 minutes. The efficiency in the three digesters was however within the same range and the heating value of the biogas improved by 66%. The flow rate was maintained at 20 litres/min to allow adequate contact time between the raw gas and the adsorbent materials in the purification system. The reduced heating time was an indication of an improved CV of the biogas as a result of passing the raw biogas in the purifications.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The study aimed at developing a biogas purification system as well as both sampling at test the best flow rate for this process and determining the CV of the resulting gas. Based on the results, it can be deduced that the quality of biogas produced was improved by reducing the H_2S and CO_2 content of the biogas to a considerably low concentration after purification. The results showed that the combination of adsorption and absorption removed the contaminants with an efficiency of up to 20%. The findings confirmed that the use of ferric oxide, lime/limewater and silica gel has significant influence in the improvement in quality of biogas. With the average inlet H_2S concentration of about 0.005% passing through the adsorption unit, the tests showed that the H_2S levels reduced to 0.002% with a reasonably minimal time of 15 minutes for a flow rate of 20 litres/min. The $Ca(OH)_2$ solution guaranteed CO_2 reaction in the biogas intensively through an acid-base neutralization reaction absorbing and reducing the CO_2 gas. This resulted in upgrading of the CH_4 to a level of about 25% and a decrease in the CO_2 to the tune of about 20%. Upgrading biogas enriched it with CH_4 concentration from an average of 48% to 60%. The improvement in the heating value of the biogas was found to be 66%.

In summary, the adsorption process reactor is simple and cheap as the materials required are readily available and good results were achieved for the removal of CO_2 as well as H_2S from the biogas. Results from the study suggest that the gas could provide additional benefits to farmers. The purification system can successfully be integrated with the digester plant at a cost of about Ksh 6,000.

5.2 Recommendations on Further Work

Combustion of fuels that contain hydrogen sulphide gas produces toxic fumes that result to respiratory ailments such as bronchitis and asthma. The solution to this is therefore removal of such contaminants. This study recommends that reactors for the removal of biogas contaminants be built alongside biogas digesters to ensure the safety of the environment and wellbeing of the consumers.

Further research may help explain the influence of the derived adsorption materials quality on the results towards improving reliability of the reactor.

i. Further tests should be performed both on site as well as in the laboratory at controlled conditions to verify the contaminants removal rate.
ii. More tests should be conducted in determining the performance of the purifying agents to verify influence on biogas heating value.

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APPENDIX 1 MATERIALS LIST AND RESPECTIVE COSTS FOR BIOGAS PURIFICATION REACTOR

Item	Description	Quantity	Unit Cost KSh.	Total Price KSh.
PVC pipe	Φ = 75 mm, length = 150 mm	2 Nos.	150	300
PVC pipe	Φ = 50 mm, length = 150 mm	2Nos.	100	200
Isolation Valves	Φ = 10 mm,	7Nos.	150	1,050
PVC hose pipe	Flexible pipe Φ = 10 mm	1.5 m	100	150
PVC Elbows	Φ = 20 mm	4 pieces	20	80
PVC Tees	Φ = 20 mm	2 pieces	25	50
PVC Plug	Φ = 75 mm	2 pieces	95	190
PVC Plug	Φ = 50 mm	2 pieces	65	130
Support Clip	Φ = 75 mm	2 pieces	40	80
Support Clip	Φ = 50 mm	2 pieces	30	60
PVC Nipple	Φ = 10 mm	8 pieces	15	120
Self tapping screws	¾’ x 1’	8pieces	10	80
Brock Board	1 m x 0.2 m x 15 mm thick	1 piece	200	200
Ferric Oxide Pellets		750 gm	1500	1500
Calcium Oxide		100 gm	100	100
Silica Gel		150 gm	250	250
labour			30% of materials cost	745
Grand Total				**Ksh. 5,902**